Commercial AED instrumentation, with a detection limit of ca. 250–400 pg, has been too insensitive for the determination of CBs in all but the most contaminated samples. Recent AED development has used a 350 kHz on-column RF plasma set at 837.6 nm for the Cl emission operating at 350°C with He at 10 mL min$^{-1}$ as make-up gas and $O_2$ as the plasma dopant. The capillary column is positioned so as to sustain the plasma *inside* the end of the column. This ‘on-column’ configuration improves the detection limit by × 30 and provides sufficient sensitivity to be compared directly with the ECD in the analysis of real sediment samples.

*See also:* **II/Chromatography: Gas:** Detectors: Mass Spectrometry; Detectors: Selective; Multidimensional Gas Chromatography; Sampling Systems; **Extraction:** Solid-Phase Extraction. **III/Insecticides:** Gas Chromatography; **Pesticides:** Gas Chromatography.

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# POLYCYCLIC AROMATIC HYDROCARBONS

## Gas Chromatography

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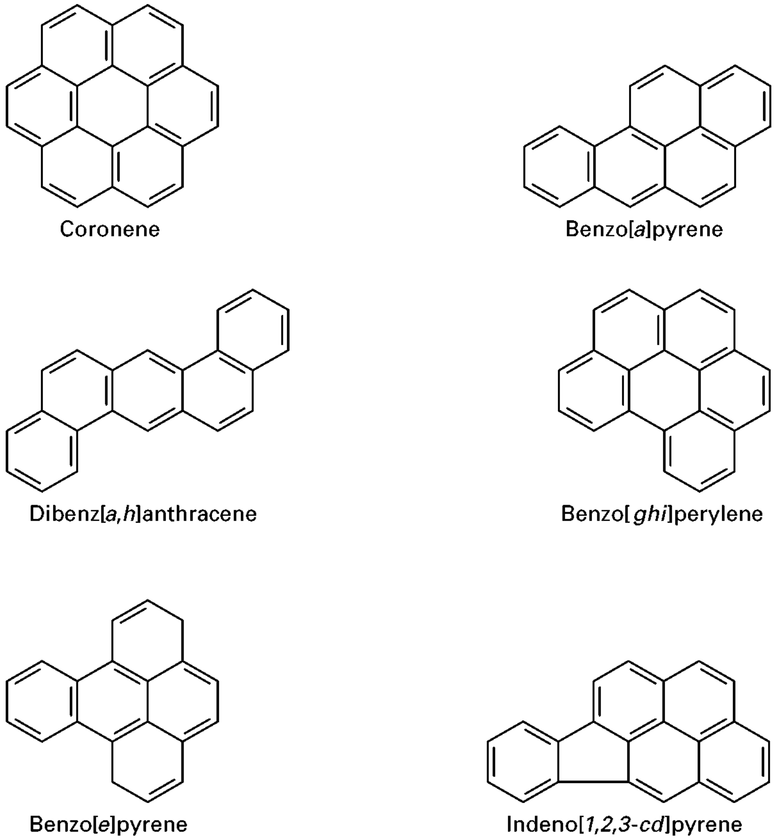
## Introduction

Polyaromatic hydrocarbons (PAHs) constitute a very extensive and probably the most structurally assorted group of organic compounds. They are ubiquitous to the environment, and may well be the most widely studied class of environmental pollutants. Unfortunately, because of their diverse nature, there is no single nomenclature that describes collectively these compounds to everyone’s satisfaction. Thus, one is likely to come across the terms polyaromatic hydrocarbons, polyaromatic compounds, polynuclear aromatic hydrocarbons or polycyclic aromatic hydrocarbons in the scientific literature, even though all may actually be referring to this same class of chemicals. For the purpose of this article, PAH is used in the broadest sense possible, so that even those compounds that contain atoms other than carbon and hydrogen may be included in the discussion.

PAHs are formed primarily from the combustion of fossil fuels, with major sources being of anthropogenic origin, although bacteria and plants also contribute some PAHs to the environment. Interest in these compounds dates back to 18th-century England when it was suggested that scrotal cancer afflicting chimney sweeps could have been caused by substances present in soot from burning coal. PAHs were still unknown at that time, of course. It was only 150 years later, in the 1930s, that it was finally confirmed that soot contains benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene, two PAHs with carcinogenic properties. Research into PAHs was given significant impetus by this discovery and, to this day, enormous interest is still focused on these compounds, not only in studies



Coronene

Benzo[*a*]pyrene

Dibenz[*a,h*]anthracene

Benzo[*ghi*]perylene

Benzo[*e*]pyrene

Indeno[*1,2,3-cd*]pyrene

**Figure 1** Structures of some common polyaromatic hydrocarbons.

on chemical carcinogenesis, but also in analytical science, for which PAHs have become favoured test analytes. Befitting their status as important pollutants, the US Environmental Protection Agency has designated 16 PAHs as priority pollutants. **Figure 1** shows the structures of some common PAHs.

PAHs are found in a variety of environmental samples (airborne particulates, water, soil) and even in food cooked at high temperatures (grilled meats and fish, for example). Moreover, they are often present as complex mixtures containing dozens of components. It is therefore essential to analyse for PAHs in environmental and other samples to which the human population in particular may be exposed.

Why we need to identify and quantify PAHs in such samples is clear. Since many but not all PAHs are carcinogenic and/or mutagenic, and complex mixtures normally contain both types, the only way to assess the risks posed by those with high carcinogenic potential is to characterize them individually. Additionally, the type and variability of different combustion sources produce PAH profiles (in terms of the composition and quantities of the individual compounds) that are characteristic of their origins. For instance, motor vehicle exhaust fumes contain relatively more benzo[*ghi*]perylene, coronene and cyclopenta[*cd*]pyrene than any other sources. Thus, careful examination of such profiles can help to identify the PAH source, and health control steps can be taken to reduce or even eliminate emissions from the particular source. To be able to provide accurate information on individual PAH components in complex mixtures, a technique with good separation capability is imperative. Coupled with its other advantages, such as reasonably fast analysis and sensitivity, gas chromatography is most appropriate for PAH separation. This article focuses on the application of gas chromatography to the separation of PAHs. Attention is placed on the use of capillary columns since analysis by packed columns of such complex mixtures is impractical.

## General Considerations

To be separated by gas chromatography, compounds must be volatile and thermally stable within the range of temperature used in the analysis. In this respect, PAHs conform to the requirements, since those containing up to about 24 carbon atoms are amenable to analysis by the procedure. There are exceptions, of course, since volatilities do vary, even for compounds with the same carbon number.

The value of high resolution gas chromatography for separating complex multicomponent PAH mixtures was first recognized in 1964. This was the first application of capillary column gas chromatography to PAHs. Today, this technique remains the most amenable, and therefore the method of choice, for separating these compounds. Fortuitously, it has been ascertained that virtually all of the PAHs that have been found to be carcinogenic or mutagenic are also relatively volatile – thus, gas chromatography is the method of choice to analyse for them, especially if based on considerations of cost and ease of use.

The application of capillary gas chromatography to PAH analysis took a leap forward in the 1970s when several column pretreatment procedures were devised to overcome the problems associated with coating liquid phases on glass column wall surfaces. Columns coated by surface adsorption were not easily reproducible. For high efficiency separations the coating of the liquid phase should be a thin, uniform film; complete coverage of the surface is also essential to counter active sites which compromise chromatographic integrity. One way of achieving satisfactory surface modification was by acid-leaching the Lewis acids present in the glass used to manufacture columns; much improved chromatography was the result.

General improvements in gas chromatography in relation to high efficiency separations have gone hand-in-hand with PAH analysis. Mention was made above of these compounds being commonly used as test substances to evaluate new or improved analytical procedures. This is because of the interest in their carcinogenic properties, their widespread environmental occurrence and their availability as multicomponent standard mixtures.

An early illustration of the power of capillary gas chromatography for separating complex mixtures of PAHs was provided by work published in the mid-1970s. More than 20 PAHs, including sulfur-containing compounds, present in carbon black from petroleum feedstocks were separated on a capillary column coated with SE-52 (5% phenyl methylsilicone gum) stationary phase (**Figure 2**). Isomers and trace compounds not previously detected could be resolved.

Subsequent work further illustrated the excellent resolution capillary columns could offer when more than 100 PAHs (including alkylated compounds) isolated from airborne particulates were separated. Interestingly, isomers differentiated only by alkyl group positions could be well resolved.

Further improvements in PAH analysis have subsequently come in the form of newer stationary phases, especially those with increased thermal stability. Chemically bonded and cross-linked polymeric phases were introduced in the early 1980s, along with

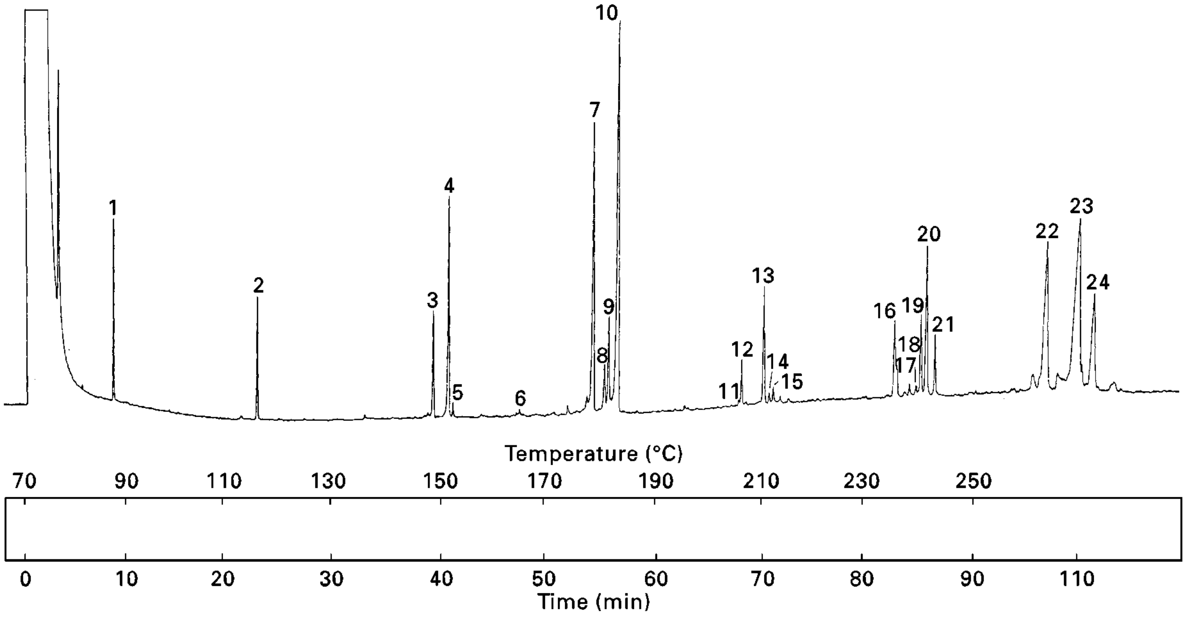


**Figure 2** Chromatogram of PAHs, including sulfur-PAHs (peak 9, benzo[*def*]dibenzothiophene; peak 11, benzo[*a*]dibenzothiophene) in extract of furnace black from petroleum feedstocks. (Reproduced with permission from Lee ML and Hites RA (1976) Characterization of sulfur-containing polycyclic aromatic compounds in carbon blacks. *Analytical Chemistry* 48: 1890–1893.)

columns made of fused silica. They allow analyses to be performed at elevated temperatures, in contrast to physically coated columns. These phases also have greater wettability characteristics, meaning that, even at high temperatures, their homogeneity is maintained, and they do not collapse into droplets. Chromatographic data are more consistent and reliable as a result of these improvements; this is an important consideration if information about composition and identity is needed from environmentally derived PAH samples.

Methylsilicone stationary phases have been most commonly employed for separating PAHs; these include SE-30, OV-1, OV-101 and SP-2100. Others that provide good performance, like SE-52, referred to above, are based on the same material. Some examples of these are SE-54 (1% vinyl, 5% phenyl methylsilicone), OV-3 (10% phenyl methylsilicone), OV-7 (20% phenyl methylsilicone) and OV-17 (phenylmethylsilicone). Of these, SE-52 and SE-54 have perhaps been the favoured stationary phases of most people working on PAH analysis. Commercial suppliers now list many phases under their own labels that are equivalent or nearly equivalent to those mentioned above and that are optimized for PAH analysis.

Liquid crystalline stationary phases have also played a role in the history of PAH analysis by gas chromatography. They offer the promise of separating closely related PAHs with greater efficiency than conventional stationary phases. The motivation for applying such phases was the complexity of PAH mixtures, especially in relation to isomers which differ significantly in their carcinogenic properties (e.g. benzo[*a*]pyrene which is carcinogenic and benzo[*e*]pyrene which is less so, and benz[*b*], [*j*] and [*k*]-fluoranthenes which possess a range of carcinogenic activities). Liquid crystal phases seemed to be most suited to packed-column gas chromatography since it was the latter (with conventional stationary phases) that lacked the capability to separate closely related components.

The rationale for using liquid crystal packings is that, in comparison to conventional phases they are better able to exploit slight structural differences in isomeric PAHs, thus enabling their resolution. Separation is based on relative permeation of differently shaped PAH between layers of the liquid crystals.

Despite demonstration of some impressive results with liquid crystal phases, the advent of capillary columns, coupled with improvements in conventional stationary phases, column treatment and column coating technologies have led to a slight loss of interest in these phases, not only for separating PAHs but also other analytes. (Such phases have been coated onto capillary columns and are still sporadically utilized for PAH analysis.) The main disadvantages of these phases are that their properties tend to change over prolonged use, and long equilibrium times are needed between runs, although newer phases have higher thermal stabilities and tolerance. Additionally, PAH retention behaviour appears to be extremely difficult to predict, and expectations based on knowledge of retention of very similar PAHs are often at variance with subsequent experimental observations.

## Applications

Some of the more important applications of gas chromatography to PAH analysis have been in atmospheric pollution studies. As heavy traffic densities and industrial pollution are a common feature in major cities of the world, the carcinogenic and mutagenic potential of airborne particulates in urban atmospheres has attracted increasing attention. PAHs are commonly emitted into the atmosphere adsorbed on particulate matter from major combustion sources such as motor vehicle engines via their exhaust systems, uncontrolled natural or deliberate burning of forests, wood and coal, refuse, domestic and industrial power and heat generation. The most convenient method of collecting particulate samples is by drawing contaminated air through a filter. The entrapped particulates are then extracted for their PAH content. Another popular method is to trap PAHs directly on adsorbents (e.g. polyurethane plugs), which are subsequently extracted. Various procedures of extraction include Soxhlet extraction with a suitable organic solvent, followed by additional clean-up steps to isolate the PAH fraction. Other, more rapid extraction methods such as supercritical fluid extraction, accelerated solvent extraction and microwave-assisted solvent extraction have been introduced, the latter in particular has become very popular in recent years.

Although the flame ionization detector (FID) is commonly used for PAH analysis, its universality of response and thus lack of selectivity dictate that after sample extraction careful and sometimes laborious clean-up procedures must be performed to isolate the PAH fraction before gas chromatographic separation. The electron-capture detector (ECD) has also been used for PAH analysis, and ECD-FID response ratios can be calculated and used to differentiate between PAH of similar structures. **Figure 3** shows a chromatogram of PAHs extracted from urban air-borne particulates, generated by the two detectors simultaneously. The FID (lower trace in the figure) and ECD (upper trace) complement each

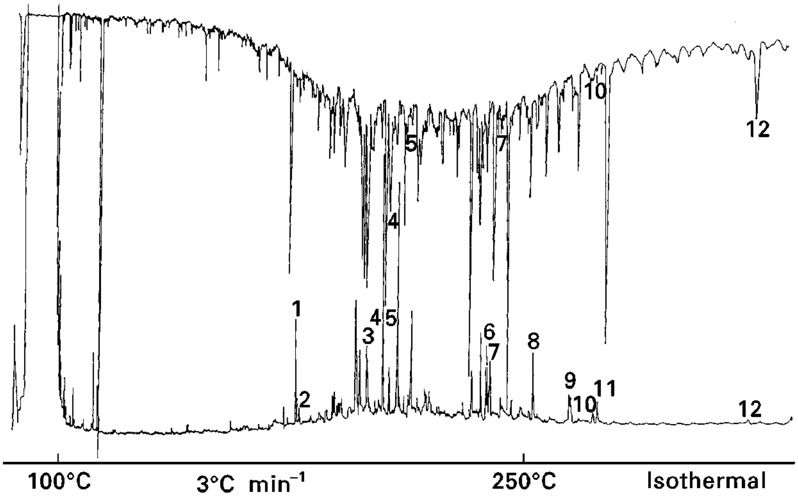


**Figure 3** Chromatogram of polyaromatic hydrocarbons from urban particulates generated from simultaneous (bottom) flame ionization and (top) electron-capture detection (FID and ECD). Peak identities: 1, Phenanthrene; 2, anthracene; 3, 3,6-dimethylphenanthrene; 4, fluoranthene; 5, pyrene; 6, benz[*a*]anthracene; 7, chrysene/triphenylene; 8, $\beta,\beta$-binaphthalene; 9, benzo[*j*] and [*k*]fluoranthene; 10, benzo[*e*]pyrene; 11, benzo[*a*]pyrene; 12, *o*-phenylpyrene. (Reproduced with permission from Bjorseth A and Eklund G (1981) Analysis of polynuclear aromatic hydrocarbons by glass capillary gas chromatography using simultaneous flame ionization and electron capture detection. In: Bertsch W, Jennings WG and Kaiser RE (eds) *Recent Advances in Capillary Gas Chromatography*, pp. 477–490. Heidelberg: Dr Alfred Hüthig Verlag.)

other to provide more positive identification of the PAHs.

Increasingly, mass spectrometry as a gas chromatographic detector is assuming greater importance for most PAH applications because of its greater sensitivity in quantitative analysis (based on its selected ion-monitoring mode in which ions that are characteristic of particular components are monitored) and improved diagnostic power. Using mass spectrometry with less drastic ionization conditions (chemical ionization, negative ion chemical ionization, etc.), similar or isomeric PAHs can be identified with greater certainty, in contrast to electron impact ionization which normally cannot be used to differentiate between such PAH structures since they often give nearly identical mass spectra. In addition to FID, ECD and mass spectrometry, other detectors have been coupled to gas chromatography for PAH analysis. These include the Fourier transform infrared detector, the photoionization detector, the photometric detection and the nitrogen-specific chemiluminescence detector – all of which respond to certain elements or functionalities in compounds, and thus afford a measure of selectivity.

Particulates emitted from vehicles that use diesel fuel have been found to have significant mutagenic potential due to the presence of the nitro-PAHs such as nitropyrenes, nitrofluoranthenes, dinitropyrenes, hydroxynitropyrenes and acetoxynitropyrenes. Some evidence suggests that there may be some other as yet uncharacterized compounds present in diesel particulates that are mutagenic but do not belong to the nitropyrene family. Evidence of diesel particulates having greater mutagenicity than other types of particulates normally found in urban atmospheres has also been reported, based on results of a study carried out in a Japanese city. Some previously unknown mutagens were detected and identified; these included PAHs containing $NO_2$ substituents as well as a nitrogen atom in the ring nucleus. The discovery of these compounds underscores the enormous complexity and diversity represented by the family of PAHs.

In recent years, the size of airborne particulates has become a major issue in the assessment of the health risks posed by these atmospheric pollutants. For example, smaller-sized particles can be transported over greater distances, since they take longer to settle, if at all, increasing their transboundary pollution potential. They are also more easily inhaled, and are therefore more hazardous to health. There has been research to determine the link between particle size with the PAH composition associated with it. If a link can be determined, the health effects of various-sized particles can be better understood and studied. This may allow more effective control of emissions of PAHs to be implemented, by focusing on the emission sources with which particular groups of PAHs are associated. The gas chromatograms of PAHs associated with particulates of sizes $< 0.5$ μm and $> 7.2$ μm are shown in **Figure 4**. It is observed that the two chromatographic profiles are significantly different.

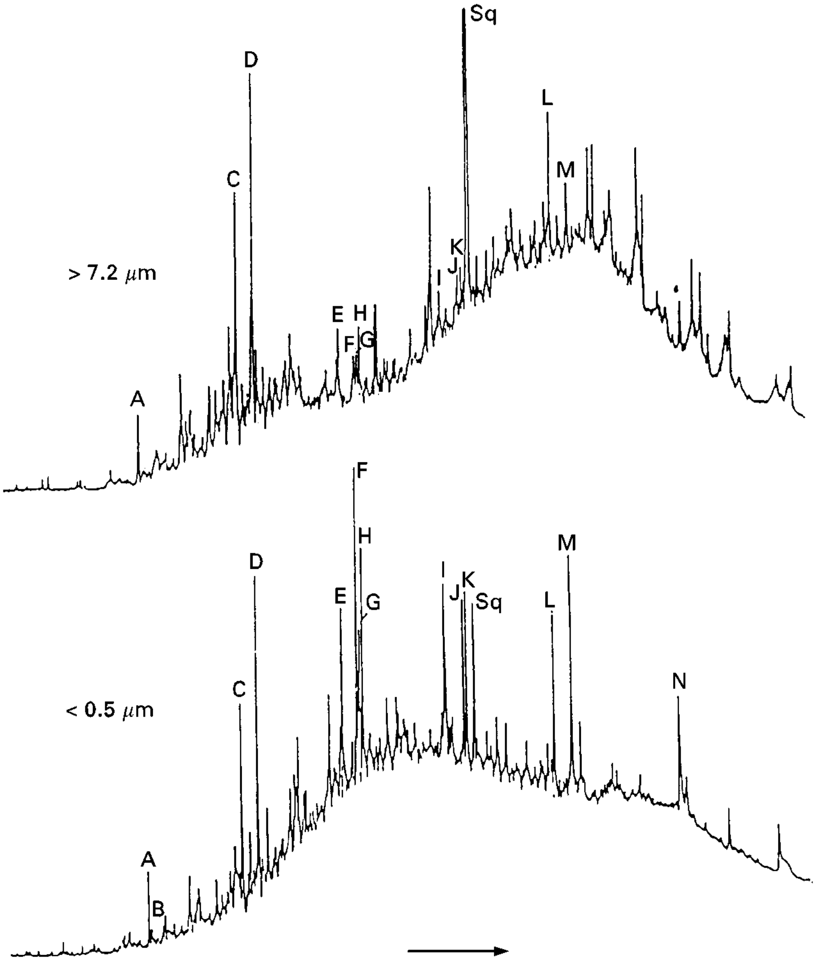


**Figure 4** Chromatogram of the aromatic fraction of urban particulates. Top trace: extract from particulates of size > 7.2 μm. Bottom trace: extract from particulates of size < 0.5 μm. Peak identities: A, Phenanthrene; B, anthracene; C, fluoranthene; D, pyrene; E, benzo[*ghi*]fluorene; F, 4(*H*)cyclopenteno[*cd*]pyrene; G, benz[*a*]anthracene; H, chrysene/triphenylene; I, benzo[*b*] and [*f*]fluoranthene; J, benzo[*e*]pyrene; K, benzo[*a*]pyrene; L, indeno[*1,2,3-cd*]pyrene; M, benzo[*ghi*]perylene; N, coronene; Sq = squalene. (Reproduced with permission from Aceves M and Grimalt JO (1993) Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environmental Science and Technology* 27: 2896–2908.)

The urban atmosphere is only one of the environmental classes in which information on PAH is of interest. Much work has been done, and is continuing, on industrial effluents, and workplace and indoor atmospheres. Interesting insights on indoor PAH pollution have resulted from studies carried out by gas chromatography. Emissions from home appliances such as natural gas space heaters and water heaters have been found to contain PAHs, including the oxygen, nitrogen and sulfur analogues. Such findings are significant because they draw attention to the PAH exposure faced by young children and non-working adults in domestic dwellings. The comment has been made that more attention should perhaps be focused on such indoor pollution by PAH by health authorities than hitherto. **Figure 5** shows a reconstructed total ion mass chromatogram for exhaust emissions from home appliances using natural gas. Samples were collected on a main filter and a backup filter.

Another form of indoor pollution far removed from urban or suburban settings may also be important. In rural communities, wood, charcoal or coal combustion in open stoves is often used for cooking. In confined dwellings with little or no ventilation, exposure to the combustion products, including PAHs, represents significant risks. Indeed, in a rural commune in China, the women exhibited a high lung cancer mortality rate even though most of them were non-smokers. Using gas chromatography–mass spectrometry, researchers determined PAHs, alkylated PAHs and nitrogen PAHs in particulates collected in commune households during cooking, primarily performed by these women. In many other parts of Asia as well as in Africa, similar lifestyles are followed;

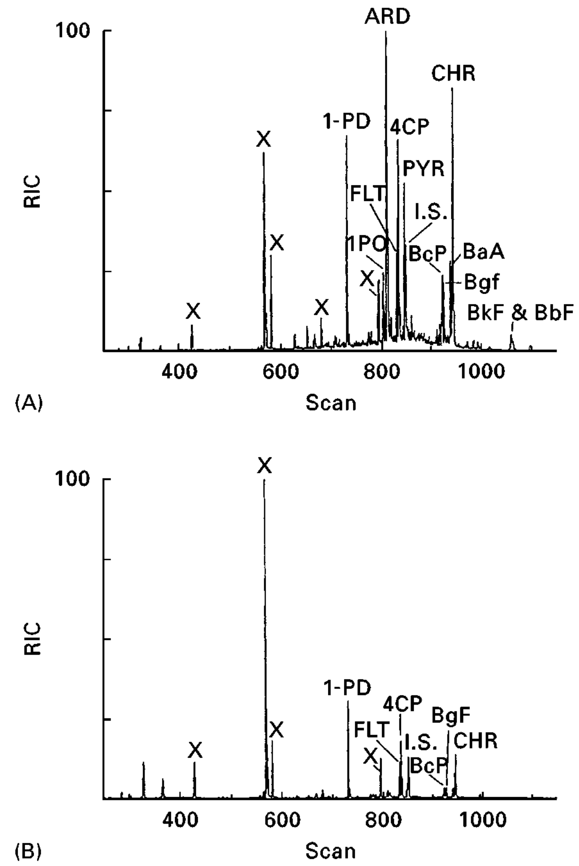


**Figure 5** Total reconstructed ion current (RIC) or exhaust emissions from natural gas-fired home appliances: (A) fine particle front filter samples; (B) backup filter samples. Peak identities: I.S., internal standard (*n*-C$_{24}$D$_{50}$); 1-PD, co-injection standard (1-phenyldodecane): 1PO, 1*H*-phenalen-1-one; FLT, fluoranthene; ARD, cyclopenta[*def*]phenanthren-4-one; PYR, pyrene; BcP, benzo[*c*]phenanthrene; BgF, benzo[*ghi*]fluoranthene; BaA, benz[*a*]anthracene; CHR, chrysene/triphenylene; BkF, benzo[*k*]fluoranthene; BbF, benzo[*b*]fluoranthene; X, contaminant. (Reproduced with permission from Rogge WF, Hildemann LM, Mazurek MA, Cass GR and Simoneit BRT (1993) Sources of fine organic aerosol, Part 5: natural gas home appliances. *Environmental Science and Technology* 27: 2736–2744.)

thus, indoor PAH pollution is a real threat that needs to be monitored more closely.

Notwithstanding the vast body of literature available on the use of gas chromatography for atmospheric PAH analysis, there has been a tremendous amount of work in other areas where information on these compounds is of interest. Capillary gas chromatography has been the major technique in the identification and determination of PAH mixtures in samples such as cooked foods, coal tar and creosote, soils and sediments, cigarette and marijuana smoke condensates, used engine oils and other oil products, carbon black, natural and contaminated waters including rain and snow, marine organisms, petroleum products, asphalt, tyre particles and other rubber products, burnt plastics, coke, shale oils, biological sewage sludge, fly ash from incinerators, and soot from a variety of sources like forest and agricultural fires.

## Concluding Remarks

Gas chromatography, particularly when used with capillary columns, has been the mainstay of separation techniques for the analysis of complex mixtures. The analysis of PAHs has virtually been intertwined with the technological progress of gas chromatography over the past few decades. Despite the introduction of other high performance separation methods such as liquid chromatography and supercritical fluid chromatography, gas chromatography has remained the technique of choice for separating PAHs in a large variety of samples. Although gas chromatography can be considered to be a mature technique, it is unlikely that its pre-eminent role in PAH analysis will be seriously challenged in the foreseeable future, even given the past and current tremendous pace of progress in analytical chemistry, particularly in separation science.

*See also:* **III / Flame Ionization Detection: Thin-Layer (Planar) Chromatography; Mass Spectrometry.**

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