

# MASS SPECTROMETRIC AND CHROMATOGRAPHIC TECHNIQUES FOR DETERMINATION OF POLYCYCLIC COMPOUNDS

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## ABSTRACT

Use of the integrated ion-current technique offers great advantages over conventional mass spectrometry. It provides a most sensitive method of analysis with limits of detection in the subpicogram region. Furthermore it can be frequently used to resolve isomeric compounds. In conjunction with other techniques it offers a great potential in the detection and estimation of air pollutants.

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## INTRODUCTION

The identification and estimation of polycyclic aromatic hydrocarbons in the atmosphere has become increasingly important following demonstration of the carcinogenic properties of some of these compounds. The presence of benzo(a)pyrene and benzfluoranthene in the atmosphere in particular has received the greatest attention in the last few years although it should be remembered that dibenzanthracene<sup>1</sup> is just as carcinogenic whilst many of the other polycyclic compounds are also moderately active. It is, therefore, highly desirable that methods for the rapid analysis of the individual hydrocarbons be developed.

Several of the analytical methods available have been reviewed by Sawicki<sup>2</sup>. Primarily they consist of isolation of the polycyclic group of compounds followed by estimation of the individual species. Column, paper and thin layer chromatography have all been used in the initial separation followed by UV absorption or fluorimetric examination<sup>2</sup>. The limits of polycyclic estimation by these methods range from the microgram region for the column chromatography/UV method to the nanogram region for the thin layer/fluorescence method.

The application of gas chromatography to the analysis of polycyclic compounds has also been developed over the last few years<sup>3-5</sup>. To some extent it has been criticized for its lack of sensitivity in that the detection limit for benzo(a)pyrene using a flame ionization detector is only approximately 5 $\mu$ g, which is very much poorer than any of the fluorimetric methods. Furthermore peaks arising from benzo(a) and benzo(e)pyrene are hardly resolved at all using conventional analytical columns<sup>6</sup>. Chromatographic methods however, have the advantage that a simultaneous analysis can be carried out for many of the more volatile polycyclic compounds.

More recently, particularly with the use of capillary columns and electron

capture detectors<sup>7</sup> the sensitivity has been increased and gas chromatography is being more frequently used as a routine method of analysis.

In a recent study involving the mechanism of formation of polycyclic compounds, during the incomplete combustion of ethylene, the advantages of using high resolution mass spectrometry in the identification and estimation of polycyclic compounds became apparent. Use of an integrated-ion current technique enabled the assay of polycyclic compounds to be made in the subpicogram range. Furthermore the shape of the ion-current curve was found to be dependent upon isomers present in the sample used.

I propose therefore to confine further remarks to a description of this method and its potential application in conjunction with other techniques.

## DISCUSSION

In quantitative mass spectrometry, it is usual, on vaporization of a sample into the source, to maintain a reservoir of sample vapour at a constant pressure while the mass spectrum is being measured or recorded. This is achieved by allowing the vapour to leak slowly into the mass spectrometer ion source so that no perceptible change in the reservoir pressure is caused. The ion current at a specific  $m/e$  value is then directly related to the partial pressure of the appropriate component in the reservoir. Absolute concentrations can then be determined by calibrating the instrument with pure samples of each component of the mixture.

Such a technique is wasteful, however, in that only a small fraction of the sample is used (<1 per cent). Furthermore the substance must be volatile enough to provide a reservoir sample pressure of several microns in order that the vapour may pass through the constriction into the ion source of the mass spectrometer.

Quantitatively, it is possible to study the mass spectra of very small amounts of sample material of low volatility by direct evaporation into the source. Such materials are evaporated from a probe which can be adjusted so as to be near the ionizing electron beam. As the partial pressure of the sample vapour within the source will vary during the evaporation process no quantitative interpretation can be made from the resulting mass spectrum.

If however, the ion current at a significant  $m/e$  value is recorded throughout the process of evaporation into the source, the area under the ion-current curve, i.e. the integrated ion-current can be related to the weight of sample evaporated<sup>8</sup>. Moreover, provided that no chemical change occurs on evaporation, the technique can be used to measure the components of a mixture by taking a series of measurements of integrated ion-current curves at several  $m/e$  values.

The very high sensitivity of this technique was first demonstrated in the estimation of metal-complex concentrations<sup>8,9</sup>.

It has now been extended to the analysis of polycyclic aromatic hydrocarbons.

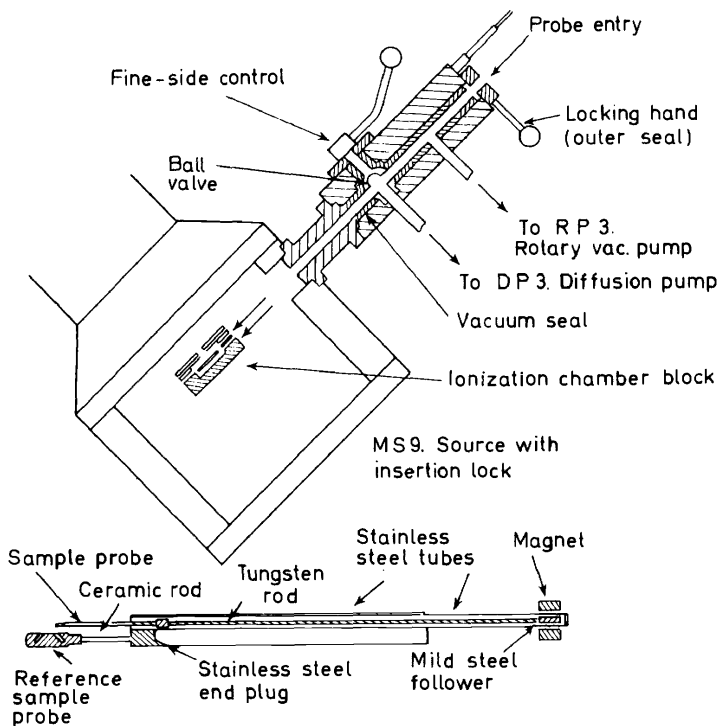
## EXPERIMENTAL

The mass spectrum of the individual polycyclic compound is first recorded by evaporating a microgram quantity into the source of the G.E.C.-A.E.I. MS 9 mass spectrometer.

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On examination of the mass spectrum a characteristic ion is selected for the quantitative examination. With the polycyclic compounds this is usually the molecular ion as it carries a very high percentage of the total ion-current.

A measured volume of the sample solution is then introduced into the sample probe (see *Figure 1*). This is then introduced into the vacuum system



*Figure 1.* MS9 Source and Direct Insertion Probe. (The probe used in this work was not fitted with a reference sample probe.)

of the mass spectrometer through the insertion lock and held in the cool part of the system until the solvent has been evaporated off. A reference compound—heptacosaffluoro-tri-*n*-butylamine is then introduced into the source by an alternative inlet, in order to calibrate the mass scale of the instrument. The sample probe is then lowered into the heated part of the source to allow evaporation of the sample whilst the rise and fall of the ion current is being recorded. *Figure 2* indicates a typical ion-current for one of the polycyclic compounds. The area under this curve is directly proportional to the amount of sample evaporated into the ion source.

## RESULTS

In order that the integrated ion-current technique may be applied successfully to the quantitative analysis of a compound, two requirements must be met. Firstly the compound must be thermally stable at the temperature

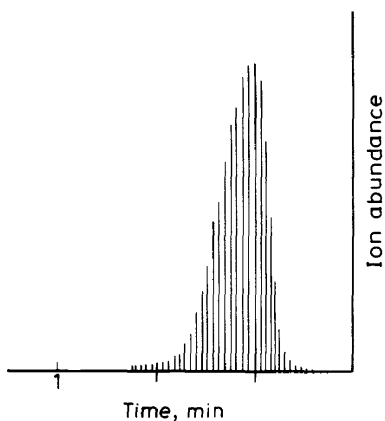


Figure 2. A typical integrated ion current curve of a polycyclic hydrocarbon.

of evaporation. Furthermore its vapour pressure/temperature relationship must fall within definite limits. Ideally at room temperature the vapour pressure must be low so that when the sample is introduced into the cold part of the vacuum system no evaporation of the compound takes place. Evaporation must take place rapidly however, when the sample is lowered into the ion source which can be heated up to  $500^{\circ}$  (see *Figure 2*).

In the main these requirements are largely fulfilled by the polycyclic compounds of higher molecular weight than phenanthrene. *Figure 3* shows a series of calibration curves for typical polycyclic compounds using quantities in the nanogram range. The calibration graphs were linear in all the ranges

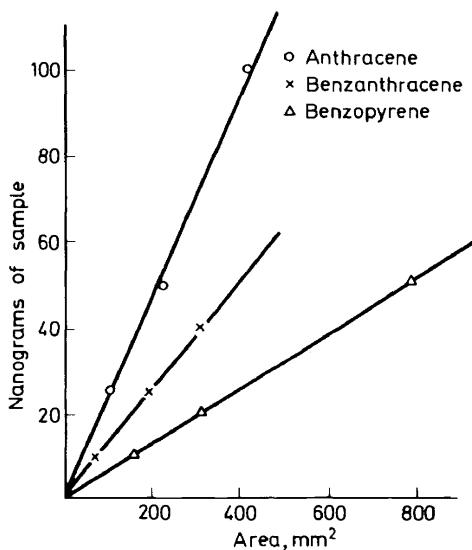


Figure 3. Integrated ion current calibration curves.

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used. The difference in slope of these graphs is accounted for by the variation in sensitivity of the instrument to the different polycyclic aromatic hydrocarbons.

By increasing the concentrations of the solutions used, the limits of detection were found for several polycyclic aromatic hydrocarbons. In general these are in the subpicogram scale (see *Table 1*). These results do not

*Table 1.* Limit of detection of various polycyclic hydrocarbons

	<i>m/e</i>	<i>Reference Peak</i>	<i>Decade</i>	<i>Limit of Detection (g)</i>
Anthracene	178	169	1.053724	$1 \times 10^{-11}$
Benzanthracene	228	219	1.041574	$5 \times 10^{-13}$
Benzo(a)pyrene	252	231	1.091370	$5 \times 10^{-14}$
Fluorene	166	164	1.012715	$1 \times 10^{-12}$
Pyrene	202	181	1.116501	$1 \times 10^{-11}$

represent the ultimate sensitivity of the method in that further amplification of the ion current is possible. This would lower the limit of detection by at least a further two orders of magnitude.

By using successive aliquots of solution at appropriate *m/e* values the components of a mixture can be determined by this technique (see *Table 2*). Polycyclic aromatic hydrocarbons are particularly suitable for this in that the

*Table 2.* Determination of mixtures of polycyclic hydrocarbons

<i>Sample</i>	<i>Amount</i>	<i>Calculated Area from graph sq. mm.</i>	<i>Measured Area sq. mm.</i>
Benzo(a)pyrene	20 ng	310	333
Benanthracene	20 ng	132	150
Anthracene	20 ng	82	86.3

molecular ion carries a large proportion of the total ion current. The shape of the ion-current curve is indicative of the rate of sublimation of the compound into the source.

A further effect was noted, however, when the sample contained a mixture of isomers. At high temperatures only one peak was obtained but as the temperature was lowered this was split into two. A further decrease in temperature produced a much longer drawn out peak indicative of a slow rate of sublimation into the source. *Figure 4* illustrates this situation for a mixture of benzo(a) and benzo(e)pyrene.

Effectively this must represent a fractional sublimation into the ion source followed by ionization of the separate species. It has been observed before with mixtures of metal complexes containing several geometrical isomers<sup>9</sup>.

Other mixtures of isomeric polycyclic aromatic hydrocarbons that have been examined include benzanthracene, chrysene and naphthacene, (*Figure 5*) benzo(a)pyrene and perylene (*Figure 6*) and benzo(a)pyrene, benzo(e)pyrene and perylene (*Figure 7*). In the first example only partial resolution is achieved while in the latter case it is particularly significant that benzo(a)pyrene is resolved from the other two less carcinogenic compounds.

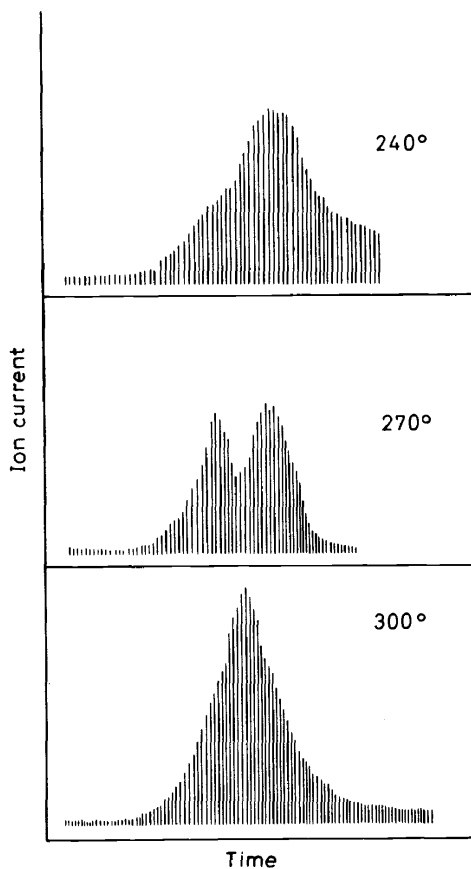


Figure 4. Integrated ion current curves of a mixture of benzo(a) and benzo(e) pyrenes.

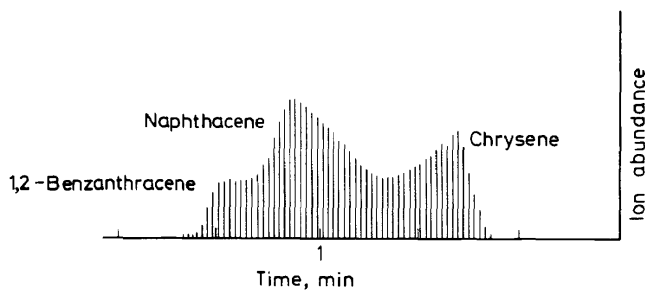


Figure 5. Integrated ion current curve for a mixture of benzo(a)anthracene, naphthalene and chrysene.

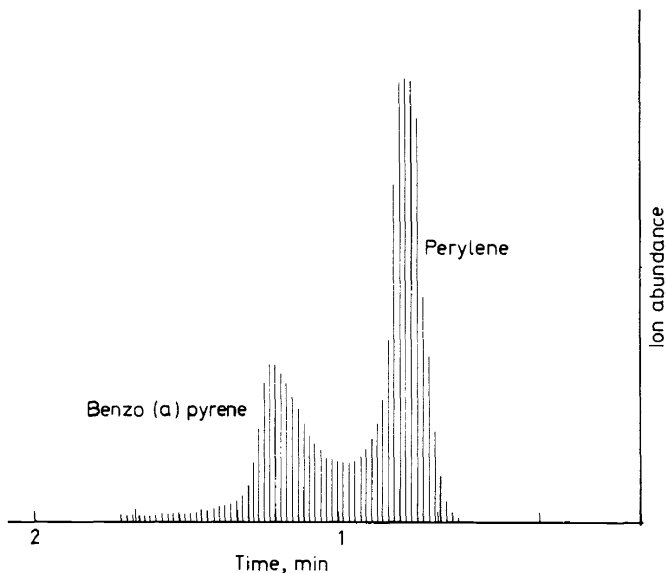


Figure 6. Integrated ion current curve for mixture of benzo(a)pyrene and perylene

In conjunction with such other techniques as gas chromatography or thin layer chromatography, this method offers great potential. Figures 8 and 9 represent gas chromatographic traces obtained for a methylene chloride extract of soot. Several peaks in these chromatograms represent mixtures of two or more substances of slightly different mass i.e. acenaphthylene/

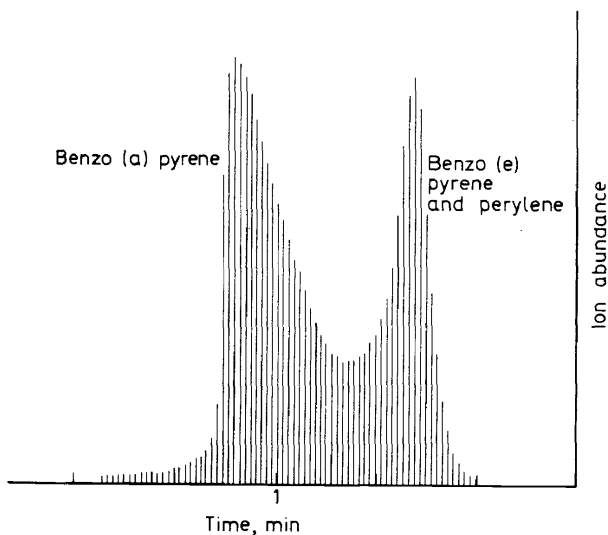


Figure 7. Integrated ion current curve for a mixture of benzo(a)pyrene, benzo(e)pyrene and perylene.

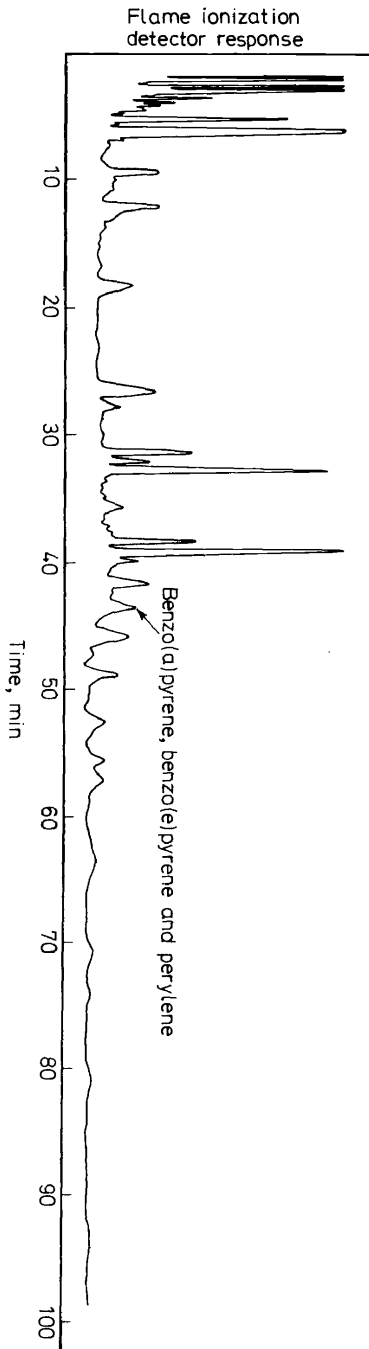


Figure 8. Gas chromatograph of soot extract (a). Temperature programmed 70° up to 250° at 6° per min. Held at limit.



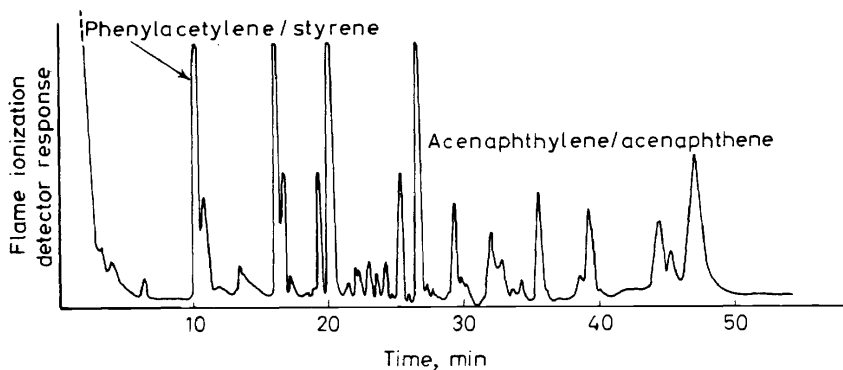


Figure 9. Gas chromatograph of soot extract (b). Temperature programmed 70° up to 250° at 6° per min. Held at limit.

acenaphthene or phenylacetylene/styrene mixtures. Use of the integrated ion-current technique at the appropriate  $m/e$  values would not only resolve the peaks but would accurately determine the amounts of each substance present. The sensitivity of such a technique would be even greater if the G.L.C. column were linked directly to the high resolution mass spectrometer by a molecular separator. Furthermore the technique could be used to resolve geometrical isomers such as benzo(a) and (e) pyrene after they have been separated from other materials by gas chromatography (see Figure 8).

In a similar way it could be used as a highly sensitive method of assay in conjunction with thin layer or column chromatography.

### ACKNOWLEDGEMENT

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