Heated Flow-Cell for Gas Phase UV-Visible Detector in Gas Chromatography of Polycyclic Aromatic Hydrocarbons

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Key Words

Gas chromatography
Polyciclic aromatic hydrocarbons
UV-visible detector

Summary

A detection system for gas chromatography based on gas-phase, molecular absorption measurements is presented, in which the chromatographic column is directly joined to the spectrophotometer flow cell, without heated transfer lines. To maintain polyciclic aromatic hydrocarbons (PAHs) in the gas phase during detection an aluminium heater was constructed. A mixture of 13 PAHs was then separated and analyzed. Parameters affecting separation (temperature program and carrier gas flow) were studied and a program designed to modify the measurement wavelength during the chromatography. The analytical characteristics of each compound were calculated, obtaining detection limits 0.2–1.5 μg mL^{-1}. Given that some compounds overlaped, it was necessary to resolve their peaks mathematicaly. Finally, the method was applied to a certified synthetic mixture, with good results.

Introduction

The determination of PAHs has been the subject of much study over the last 30 years. The bibliography makes it clear that the analytical capacity offered by individual techniques can only give partial information or can only be applied to simple samples.

For more complex real samples, the use of prior separation techniques is necessary. Many different types of chromatrographic techniques have been tried, from thin-layer chromatography (generally undertaken with fluorimetric detection [1] or even mass spectrometry (MS) [2]) to supercritical-fluid chromatography [3]. There is no doubt, however, that the best possibilities are offered by gas chromatography (GC), with flame ionization detection (FID) [4] or MS [5] and high-performance liquid chromatography (HPLC) with UV-visible detection (MAS), MS [6] or fluorescence [7]. The combination of both techniques [8,9] is also possible.

GC-FID has the disadvantages of the detector nil identification capacity and its limited sensitivity. Despite its high sensitivity, HPLC used with a fluorescence detector is not suitable for non-fluorescent PAHs or which have a low quantum yield (such as acenaphthylene). In addition, it is prone to quenching effects due to energy transfer in compounds whith overlapping peaks; a common occurrence, given its lower resolution capability. GC-MS is the best alternative; however, despite the very large capacity of MS and leaving aside the problem of cost (still high for many routine-control analysis laboràtories), the method has some analytical problems which need to be corrected. The most serious of these is the effect of the solvent (leaving the detector inoperative for the first few minutes of the chromatogram), its low capacity for positively identifying some PAHs (e. g. the similarity between the mass spectra of anthracene and phenanthrene) and the lack of suitable software for the mathematical resolution of overlapping compounds. It would be useful to have available a non-destructive detector, of reasonable cost, which would allow correction of these errors when connected in series with the MS system. This detector could also be used independently of MS as an alternative to FID.

Molecular absorption spectra can help identify each compound because they are characteristic of each. Aromatic compounds usually have three absorption bands due to π-π^* transitions in the near UV; the positions and shapes of these bands can be useful for identification purposes, particularly when combined with other qualitative information such as retention times. It is well known that solution-phase spectra are significantly changed due to matrix effects, so the gas phase is the better matrix for collection of representative solute spectra. These characteristics of MAS in the gas phase (GPMAS) make it a good candidate as a GC detector.

The first GPMAS detector for GC was described about 30 years ago by Kaye [10]. Samples emerging from the chromatograph were conveyed to an absorption cell in

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the spectrophotometer through a heated copper tube. The system worked at a fixed wavelength of about 164 nm. Since this study, new papers have appeared from time to time, in which the instrumental system used has been based on one of four differing possibilities. The first and most frequent of these is the use of a heated connection between the chromatograph and a conventional spectrometer [11,12]. The second is the modification of a detector used in gas chromatography so that it is capable of making measurements in GPMAS [13]. The third is the design of a system aimed specifically at operating as a GPMAS detector in GC [14–16]; recently Lagesson et al have designed a novel GC-UV instrument, to be comercially produced [17]. Finally, an LC detector can be used once suitably modified [18]. We have published details of simple and inexpensive system using GPMAS as a GC detector based on the use of part of the chromatographic column as a transfer line between the chromatograph and the detector, thus largely avoiding resolution loss [19–21]. This system is very useful for low boiling compounds. To apply it to PAHs, a system had to be constructed which would allow heating of the spectrometer flow cell to the temperature required; this is the system described here.

Some of the papers using GC-GPMAS have been directed towards determination of PAHs. However, it was not possible to realise the full potential of the technique until photo-diode detectors were developed. On the one hand, these instruments permit very rapid measurement of absorption spectra; using these results after suitable mathematical treatment, it is possible to resolve overlapping compounds adequately, as will be seen here. There is, however a sensitivity problem; the diode arrays generate relatively high noise (although newer instruments now appearing are starting to correct this). The use of averaging and smoothing of data makes it possible to improve the signal to noise ratio in a simple way, thus improving detection limits. Finally, molecular absorption spectra of some compounds can compliment mass spectra when making identifications, mainly when the far-UV region is used [17].

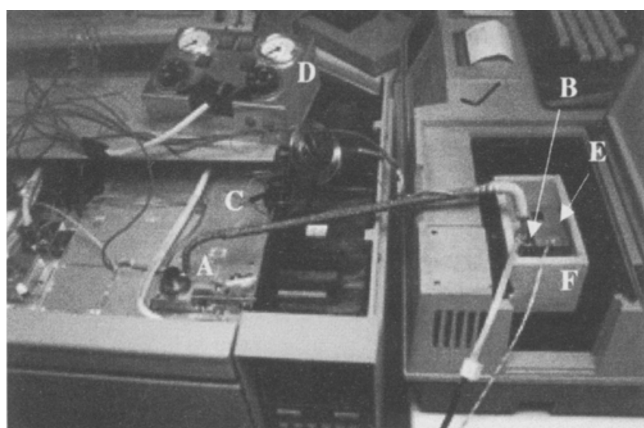

Figure 1
Photograph of system (see explanation in text).

Experimental

Instrumentation

The apparatus used is identical to that described in a previous paper [22] The carrier gas was ultrapure nitrogen at 22 mL min^{-1}. 50 μL of sample was injected. The optimised oven program consisted of holding the temperature at 170 °C for 3 min, followed by an increase at 10 °C min^{-1} to 280 °C then holding temperature for 8 min.

A system to heat the flow cell was designed to avoid the possibility of high boiling compounds condensing in the cell.

Reagents

All chemicals used were analytical reagent grade. Solutions of naphthalene, acenaphthylene, acenaphthene, phenanthrene, fluorene, fluoranthene and chrysene were prepared in petroleum ether. Anthracene, benzo(k)fluoranthene, benzo(a)pyrene, benz(a)anthracene and benzo(b)fluoranthene were dissolved in chloroform.

Solutions more dilute than these compounds were prepared in petroleum ether.

System Description and Procedure

Figure 1 shows a photograph of the system.

The end of the chromatographic column (about 20 cm) was taken outside the oven, through a hole close to the detector (A), and connected directly to the spectrophotometer cell (B).

The part of the chromatographic column (C) making the joint between the chromatograph itself and the spectrophotometer cell was wrapped in 2 m of fibreglass thread; this can be heated to a higher temperature (375 °C) using a home-made variable transformer which allowing temperature control to ± 5 °C (D).

The commercial flow cell compartment was replaced by an aluminium block (E) where the flow cell was installed. The block was heated using two cylindrical resistances and the temperature was controlled by a home-made controller, accuracy ±5 °C; the maximum temperature is 400 °C. Some aspects had to be considered before construction of the block, such as quartz and aluminium expansion, because the flow cell must fit perfectly inside the block. This aspect is very important because the cell is heated by contact with the block walls. Presence of any air between them spoils temperature control. In addition, if the cell is too loose, noise increases. The dimensions of the aluminium block shown in Figure 2 are optimum for the cell used.

To avoid damage to the spectrophotometer, the aluminium block was placed inside a box (135 × 90 × 70 mm) built of refractory material (F).

The joint between the column and the cell is of very great importance due to the high working temperatures involved; a Vyton joining was used because of its heat resistance and its inertness. Experiments have made clear the major effect from the length of the joint. A comparison was made between the chromatographic signal obtained when using a 0.5 cm joint and a second signal obtained with the column and cell entrance in contact (the Vyton tube functions only as a joint). The peak obtained from the first case was about 6 times worse than the other; in addition, the peak was very distorted; hence this distance should be as small as possible.

The spectrophotometer was not originally designed for use as a chromatographic detector. Different BASIC program had to be designed to enable the relevant measurement to be taken at each stage of the chromatogram, such as changing the measurement wavelength, reading two wavelengths and also obtaining absorption spectra from particular zones of the chromatogram. Other program also had to be designed to permit mathematical treatment of results, essentially involving smoothing over time and averaging of wavelengths.

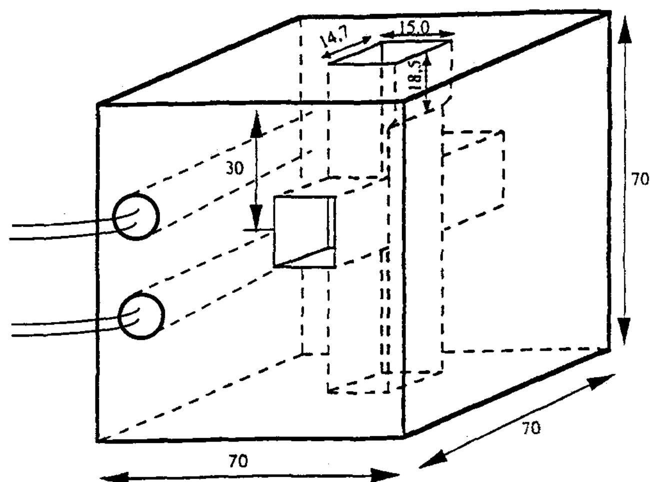

Figure 2
Schematic representation of flow cell compartment. Units in mm.

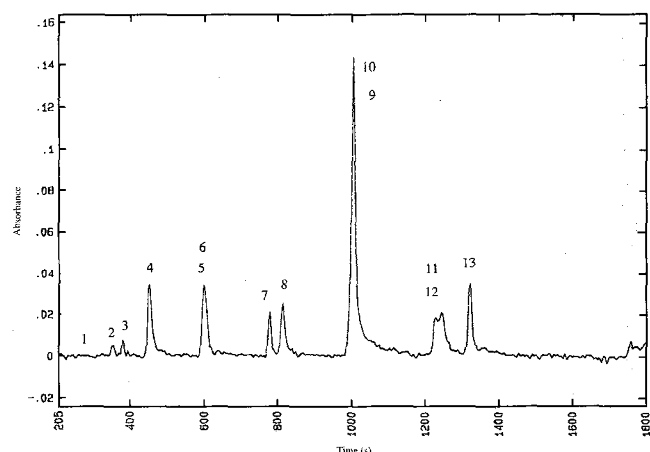

Figure 3
Chromatogram using 22 mL min^{-1} as carrier gas flow and 256 nm detection wavelength: **1** = naphthalene (no signal because no absorption at 256 nm), **2** = acenaphthene, **3** = acenaphthylene, **4** = fluorene, **5** = phenanthrene, **6** = anthracene, **7** = fluoranthene, **8** = pyrene, **9** = chrysene, **10** = benzo(a)anthracene, **11** = benzo(b)-fluoranthene, **12** = benzo(k)fluoranthene, **13** = benzo(a)pyrene.

Results and Discussion

Solvent

Correct selection of the solvent is very important if the measurement is made at a fixed wavelength, but the problem is minor if it is possible to modify the wavelength during the chromatographic process. In this case the choice of solvent would be limited only if the retention of a compound is near the retention of the solvent and the two absorption spectra are similar. Hexane and petroleum ether were tested first because they do not absorb in the UV-visible in the gas phase. Most of the PAHs are insoluble in hexane, so it was eliminated. Petroleum ether was used, although anthracene, benzo(k)fluoranthene, benzo(a)pyrene, pyrene, benz(a)anthracene and benzo(b)fluoranthene must first be dissolved in chloroform. The small quantities of chloroform used did not interfere in the chromatogram.

Temperature

This is a very important parameter which must be considered: the injector, oven, outside column and flow cell temperatures had to be optimized. The injector and flow cell temperature had to be high because of the high boiling points hence 350 °C was used as the injection temperature for all compounds. The flow cell temperature was optimized and 250 °C was enough to avoid condensation of the PAHs. No influence was observed if the flow cell was heated above 250 °C. The oven and external column were considered as a unit and kept at the same temperature.

When investigating the best separation conditions, there was difficulty in finding a wavelength common to all compounds under study. A complete investigation was therefore carried out in order to separate the compounds. The original intention was isothermal analysis, but the large number of compounds to be determined meant that the best results were using a temperature program. The program finally selected was as above (see Instrumentation).

A solution containing all the compounds was injected, using 350 °C as the injector and 250 °C as the flow cell temperatures, with 22 mL min^{-1} carrier gas flow. A chromatogram was obtained using the BASIC program described previously [18]; the measurement wavelength

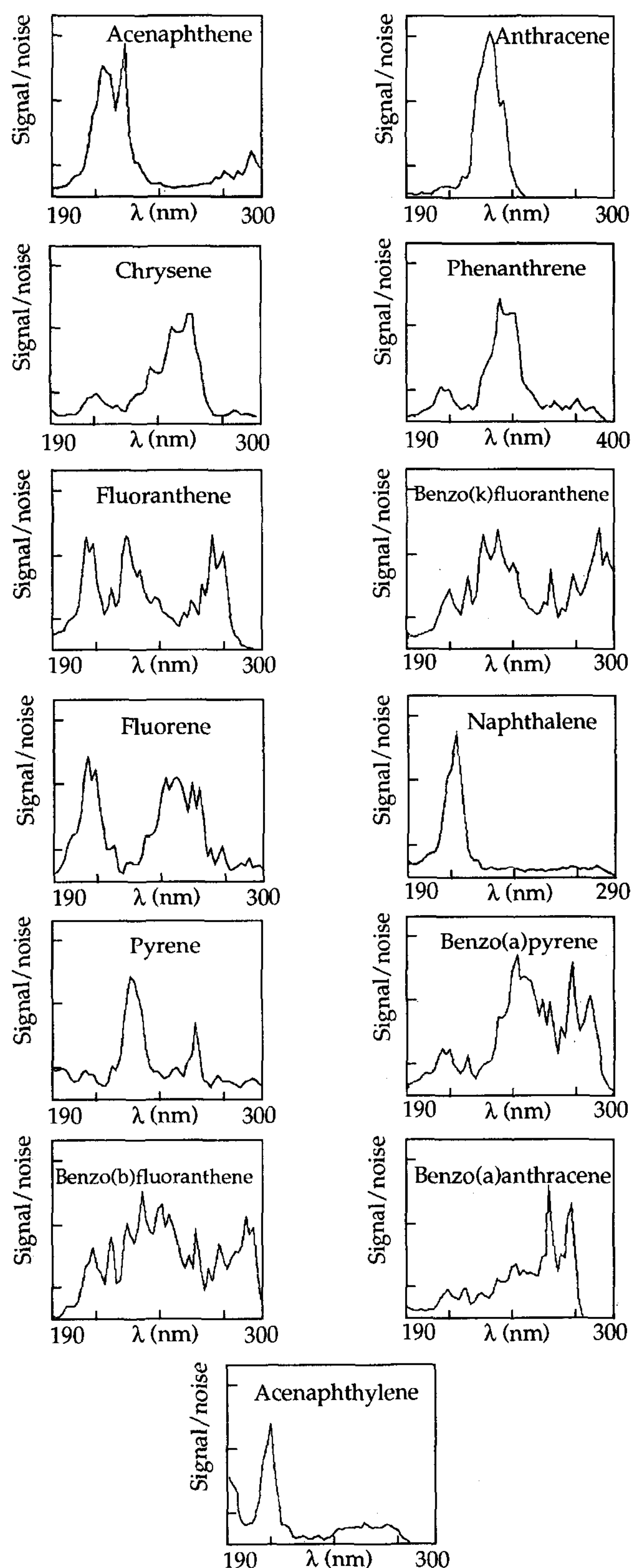

Figure 4

PAH signal-to-noise spectra obtained by dividing PAHs absorption spectra by noise spectrum.

was 256 nm. The chromatogram obtained is shown in Figure 3, which has some deficiences:

- Several pairs of compounds appear overlapped such as anthracene and phenanthrene, chrysene and benz(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene.
- There was too much dead time between some of the compounds.

These problems were not solved under any of the temperature conditions tested so this temperature rate was chosen as optimum.

Carrier Gas Flow

Since the optical spectroscopic detectors are of a concentration-sensitive type, the carrier gas flow (nitrogen) is a very important parameter affecting sensitivity and resolution. Flow rates were chosen such that the sensitivity obtained was balanced against that required for maximum chromatographic performance, best results were obtained using 22 mL min^{-1}.

Measurement Wavelength

With suitable programming of the spectrophotometer, it was possible to modify the wavelength during the chromatogram, selecting the most suitable value for each compound at each stage.

A previous study involved out a meticulous investigation of the alternatives available for increasing the signal-to-noise ratio (S-to-N) [22]. It concluded that best results are when working with the wavelength of maximum S-to-N and smoothing using a window size of 5 points.

Since this study had been carried out with a different familiy of compounds, new trials were undertaken to check that these were also the optimum conditions for the case of the PAHs.

Figure 4 shows the PAHs S-to-N spectra, from which the maximum S-to-N wavelengths were taken; these are given in Table I.

Analytical Characteristics

Calibration curves for all solutes were obtained at wavelengths with the maximum S-to-N; results are shown in Table I. Sensitivity values are the slopes of the calibration curve. Detection limits were calculated as a signal of three times the standard deviation of the noise. Reproducibility is expressed as relative standard deviation (RSD) and was obtained for five replicate determinations of the concentration shown in brackets. "Higher limit" means the higher limits of the linear response range.

Table I. Analytical characteristics for the PAHs.

Analyte	Wavelength (nm)	Sensitivity (L μg^{-1})	Detection Limit (L μg^{-1})	RSD (%)	Higher limit (L μg^{-1})
Naphthalene	212	3.34	0.6	4 (43)	200
Acenaphthene	222	2.57	0.5	3 (70)	300
Acenaphthylene	220	2.86	0.4	4 (58)	275
Fluorene	208	1.64	1.5	2 (60)	250
Fluoranthene	208	1.94	1.3	4 (46)	200
Anthracene	238	2.71	0.3	3 (48)	150
Phenanthrene	244	2.46	0.2	2 (39)	175
Pyrene	232	2.19	0.5	3 (52)	225
Chrysene	256	1.79	0.3	4 (33)	100
Benz(a)anthracene	264	1.56	0.5	3 (65)	150
Benzo(b)fluoranthene	238	0.759	0.9	4 (78)	125
Benzo(k)fluoranthene	238	0.643	1.2	4 (84)	150
Benzo(a)pyrene	256	0.829	0.6	4 (82)	125

Table II. Results obtained from the resolution of overlapping peaks

	Mixture 1 (Concentrations in mg L^{-1})		Mixture 2	
	Real concentration	Found concentration	Real concentration	Found concentration
Anthracene	98.9	100.9	45.7	41.8
Phenanthrene	99.1	92.7	38.9	36.0
Chrysene	99.9	93.1	40.8	43.7
Benz(a)anthracene	99.5	104.6	38.9	44.0
Benzo(k)fluoranthene	99.7	95.4	46.4	49.1
Benzo(b)fluoranthene	98.5	97.3	39.5	36.3

Application

Solving the Overlapping

As can be seen in Figure 3, several pairs of compounds overlap. GPMAS is able to solve this overlapping by carrying out a simultaneous determination. The concentrations of both components could be determined by resolving an equation based on the aditivity of the Lambert-Beer law. The system can be solved using high peak or area values.

Anthracene and phenanthrene appear at the same retention time; however, if the spectra are collected at that time, a spectral crossing can be seen (Figure 5). This means that one chromatographic signal, apparently resulting from just one compound, is in fact caused by more than one; it is difficult to obtain this information from other detection systems.

Since this equation can only be solved when absorbance data for mixtures and standards are collected at exactly the same time, the use of the chromatographic peak area is more satisfactory in this case. Standard solutions

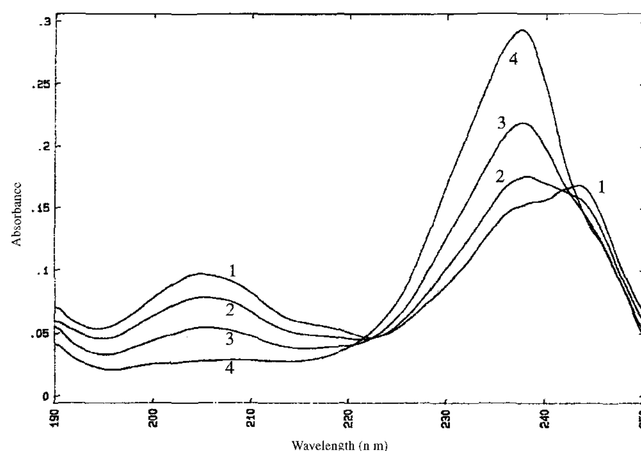

Figure 5
Absorption spectra during elution of anthracene and phenanthrene. **1** = phenanthrene (11s), **2** = phenanthrene + anthracene (19s), **3** = phenanthrene + anthracene (25s), **4** = anthracene (45s).

Table III. Results obtained from the application of GC-GPMAS to the certified sample.

	Sample 1		Sample 2	
	Concentrations (mg L^{-1})			
	Real concentration	Found concentration	Real concentration	Found concentration
Naphthalene	100.0	98.4	20.00	19.74
Acenaphthene	100.0	106.0	20.00	19.59
Acenaphthylene	98.4	105.5	19.68	20.47
Fluorene	98.1	105.5	19.62	18.96
Fluoranthene	98.2	104.5	19.64	21.10
Anthracene	98.9	100.9	19.78	20.43
Phenanthrene	99.1	93.2	19.82	18.95
Pyrene	99.1	101.0	19.82	20.90
Chrysene	99.8	94.6	19.96	21.38
Benz(a)anthracene	99.5	104.5	19.90	18.61
Benzo(b)fluoranthene	100.3	107.5	20.06	21.14
Benzo(k)fluoranthene	98.0	102.9	19.60	20.82
Benzo(a)pyrene	100.0	100.8	20.00	21.05

containing anthracene or phenanthrene and two mixed solutions were injected and measured at 242 and 238 nm. The results obtained from solving the equation system are shown in Table II.

As can be seen, two compounds that could not be separated by chromatography, can be determined using GPMAS as the detector, giving very good results. This same procedure was used for the other mixtures. In the case of chrysene and benz(a)anthracene (B(a)A), the wavelengths used were 258 nm and 276 nm. For benzo(b)fluoranthene and benzo(k)fluoranthene, the wavelengths used were 222 and 232 nm. The results obtained for two differing mixtures are also given in Table II.

Determination of a Certified Sample

The procedure described was applied to the determination of the polynuclear aromatic hydrocarbons in a Z-014G (AccuStandard Inc.) certified sample. The exact concentration of the studied compounds was about 2000 mg L^{-1}. From this sample, a further two were prepared (Sample 1 and Sample 2) by diluting 50 and 10 μL to 1 mL using petroleum ether. 50 μL samples of these solutions were injected (in quadruplicate) and measured at the maximum S-to-N wavelength, except for the overlapping compounds which were determined at the two corresponding wavelengths. The results for the two diluted samples are shown in Table III. In all cases, the RSD for each compound was < 5 %.

Conclusions

We have employed a UV-visible molecular absorption spectrophotometer equipped with diode-array as GC detector. This system has been used in the determination of PAHs with high volatilization temperatures hence it was necessary to construct a very simple system to heat the cell.

The possibilities of this system can be surmised from the results obtained and some general conclusions are:

- This detector can be selective since its wavelength can be changed.
- It is possible to determine simultaneously eluted compounds and it is possible to decide if a signal is due to one compound only or a mixture.
- This detector can give qualitative information using the molecular absorption spectra.

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