

Comparison of Element-Specific Capillary Chromatography Detectors for the Identification of Heteroatomic Species in Coal Liquids

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Abstract

A series of heteroatom-rich coal and coal-derived liquids have been analysed using gas chromatography (GC) in combination with three different element-selective detectors. Selected chromatograms, including a supercritical extract (Mequinenza lignite) and aromatic fractions isolated from coal tar pitch samples are presented. In each case a series of sulphur- and/or nitrogen-containing compounds have been identified using either flame photometric detection (GC/FID/FPD) or nitrogen-phosphorous detection (GC/FID/NPD) and the information compared with that obtained from a GC coupled to an atomic emission detector (GC-AED). Preliminary results have demonstrated the relative response characteristics of each detector and their respective ability to acquire qualitative and quantitative information in interfering background matrices. Further, due to the unique capabilities of GC-AED, a number of dual heteroatomic (sulphur-oxygen and nitrogen-oxygen) compounds have been identified.

Introduction

Polycyclic aromatic compounds (PAC) predominate in coal liquids as well as in other heavy oils derived from fossil fuels. While the polycyclic aromatic hydrocarbons (PAH) are usually the most abundant PAC, nitrogen-, sulphur-, and oxygen-containing compounds are also present in significant concentrations and their impact on processing and the environment/human health are well documented⁽¹⁻³⁾. Numerous characterisation studies have been conducted into the nature of aromatic and heterocyclic compounds present in such materials and many researchers have derived information from pyrolysis products, solvent extracts and liquefaction products⁽⁴⁻⁶⁾. Most of the recent work has focussed on the development of techniques for both separation and detection of compound or element-rich fractions. The principal methods employed to date include capillary column gas chromatography^(7,8), liquid chromatography⁽⁹⁾, element-selective detection⁽¹⁰⁻¹⁶⁾, high resolution mass spectrometry⁽¹⁷⁻²⁰⁾ and X-ray techniques⁽²¹⁾.

For the identification of heteroatomic species, the most successful approach has been the use of capillary column gas chromatography in combination with gas chromatography/mass spectrometry⁽²²⁻²⁴⁾. However, interpretation is complicated due to the properties of aromatic heterocycles being very similar to those of aromatic hydrocarbons⁽²⁾ and prior fractionation or enrichment of target compounds into compound classes is considered an essential step for their unambiguous identification^(12,13).

The use of element-selective detection in gas chromatography, for simplifying the analysis of complex hydrocarbon mixtures, is now relatively commonplace⁽²⁵⁾; but their application, particularly in the determination of trace concentrations of polycyclic

aromatic compounds, requires that due care and consideration be exercised. Flame photometric detector (FPD), has been extensively used for qualitative analysis of sulphur compounds but suffers from many inherent problems including a non-linear response (approx. quadratic) and compound dependency which makes quantitative analysis difficult and time-consuming. Moreover, quenching of the signal by coeluting hydrocarbons can considerably reduce sensitivity⁽²⁶⁾. For nitrogen compounds, the nitrogen-phosphorous detector (NPD), with a specificity (N/C) of 10^3 - 10^5 and a linear response over several orders of magnitude (see Table 1) is well suited to handling trace analysis in complex hydrocarbon mixtures⁽²⁷⁾. The relatively recent introduction of atomic emission detection (AED), as a commercially available analytical tool has received comparatively little attention⁽²⁸⁻³⁰⁾. GC-AED offers highly selective, simultaneous, multi-elemental detection and claims to suffer from none of the enigmas associated with other element-selective detectors. Based on a microwave induced plasma (MIP) and employing a moveable photodiode array (PDA) in a flat focal plane spectrometer, the AED is capable of monitoring a broad range of elements at considerably lower levels than most classical GC detectors⁽²⁷⁾. Detector response is linear and compound independent, with the possibility of empirical and molecular formula determination.

GC analysis

HP5890 Series II Gas chromatographs were used for AED and NPD analysis. A Perkin-Elmer 8500 gas chromatograph was used for FPD analysis. The GC-AED system also comprised an HP7637A Autosampler interfaced to an HP5291A AED Chemstation.

Samples were analysed by GC-AED and GC/FID/FPD using a 25m BPX-5 or equivalent column with 0.5 μ m film thickness and 0.32mm i.d. For NPD analysis a 25m SE-54 column with 0.25 μ m film thickness and 0.25mm i.d. was used. GC and AED parameters are given below:

GC parameters

Detector	FPD	NPD	AED
Injection port temperature ($^{\circ}$ C)	300	300	350
Injection mode	split (1:80)	split (1:80)	splitless
Column-detector coupling	on-line	on-line	coupled to cavity
Injection volume	1 μ l	1 μ l	0.2 or 1 μ l
Carrier gas	Helium	Hydrogen	Helium*
Oven program	Initial temp: 50 $^{\circ}$ C; Ramp rate: 4 $^{\circ}$ C/min to 280 $^{\circ}$ C; Hold: 20 min		

* High purity Helium (99.999999%) as recommended⁽²⁸⁾

AED parameters

Element	Wavelength(nm)	Scavenger gas
C	193.0	H ₂ /O ₂
S	181.4	H ₂ /O ₂
N	174.3	H ₂ /O ₂
O	777.3	H ₂ /N ₂ /CH ₄

Spectrometer purge flow: Nitrogen @ 2l/min
 Transfer line temperature: 350 $^{\circ}$ C Cavity temperature: 350 $^{\circ}$ C

Results and Discussion

The following examples illustrate the role of element-specific detectors in characterising heteroatomic species in coal liquids and demonstrate the unique capabilities of GC-AED for identifying dual or multiple heteroatom compounds in such materials. Further, from the chromatographic data accumulated to date it is anticipated that a comprehensive comparison of NPD and FPD with AED will be possible. Detailed qualitative and quantitative information is currently being obtained by a combination of literature retention time data and model compound data. Gas

chromatography-mass spectrometry (GC-MS) and GC-AED will provide structural characterisation.

From the selected chromatograms; Figure 1a,b shows the sulphur response of GC-AED and GC/FPD chromatograms respectively from the analysis of a supercritical gas extract of Mequinenza lignite. For both detectors, the chromatograms are very similar in general appearance (i.e. no. of peaks observed) and both display a series of alkyl substituted thiophenes, benzothiophenes and dibenzothiophenes. Taking into consideration sampling variations and the higher injector temperature employed in the GC-AED system the only remarkable difference is the relative peak intensities observed by both detectors. This can be accounted for by the compound dependency of the FPD and the possibility of quenching effects due to the high hydrocarbon presence.

Figure 2a,b compares the AED and NPD traces respectively for a nitrogen-rich, heat treated, coal tar pitch aromatic fraction. As anticipated from detector response characteristics for nitrogen-containing species the chromatograms are almost identical with carbazole, substituted carbazoles, benzoacridine and benzocarbazoles being observed. The NPD has the advantage of a significantly greater selectivity over carbon (see Table 1) and consequently splitless GC injections using concentrated solutions were used for AED analysis. This results in what appears to be an instrument induced effect for the high boiling heterocyclics where peak splitting and a general distortion of peak shape occurs. Similar observations have been made for sulphur and oxygen containing PACs.

The unique capabilities of the GC-AED as a multi-element detector are demonstrated by the identification of dual heteroatom compounds present in both the supercritical gas extract and the coal tar pitch sample. Figures 3a,b show segments of the C,S,O and C, N, O, chromatograms obtained for Mequinenza lignite and heat treated pitch respectively. By correlating characteristic emission wavelength responses with retention time data, the presence of oxygen-sulphur and nitrogen-sulphur compounds have been unambiguously identified. Further confirmation is obtained using a "snapshot" facility which is a selected segment of the emission spectrum showing specific elemental emission wavelengths. The exact nature of these dual heteroatom species is as yet uncertain. Figure 4 provides further evidence of the multi-element character of GC-AED where the aromatic fraction from an untreated coal tar pitch has been analysed by GC-AED for C, S, N, O (Figure 4a) and the corresponding GC/FID/NPD is shown in Figure 4b. In both cases the carbon/FID channel provides mainly evidence of nitrogen-containing species but due to the high selectivity for both sulphur and oxygen over carbon for AED (see Table 1) the presence of both sulphur and oxygen compounds (and possibly further multiple heteroatomic species) can be confirmed

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Table 1: Detector response characteristics¹

	Detectors		
	FPD	NPD	AED
Minimum detectable levels (pgS/sec) (pgN/sec)	2-50	0.05	(1-2) (50)
Selectivity (S/C) (N/C)	10 ⁴ -10 ⁵	7*10 ⁴	(8*10 ⁴) (2*10 ⁴)
Linear response	No (quadratic)	Yes	Yes
Linear dynamic range	1-5*10 ²	10 ⁵	(1*10 ⁴) (2*10 ⁴)

¹Values taken from literature⁽²⁶⁾

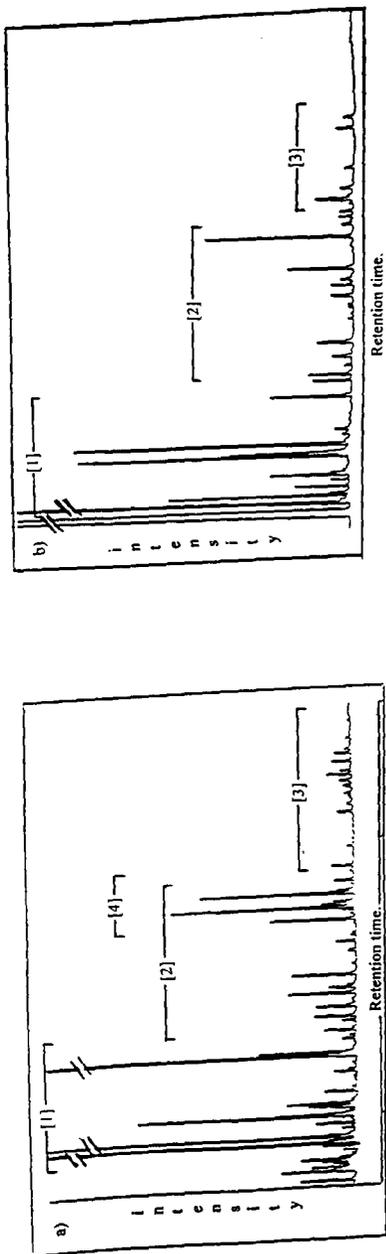


Figure 1. A supercritical gas extract of Mequinenza lignite: a) AED sulphur 181nm channel and b) FPD sulphur response. General assignments: [1] substituted thiophenes; [2] benzothiophenes and [3] dibenzothiophenes. [4] See Figure 3a) for an enlargement of this region.

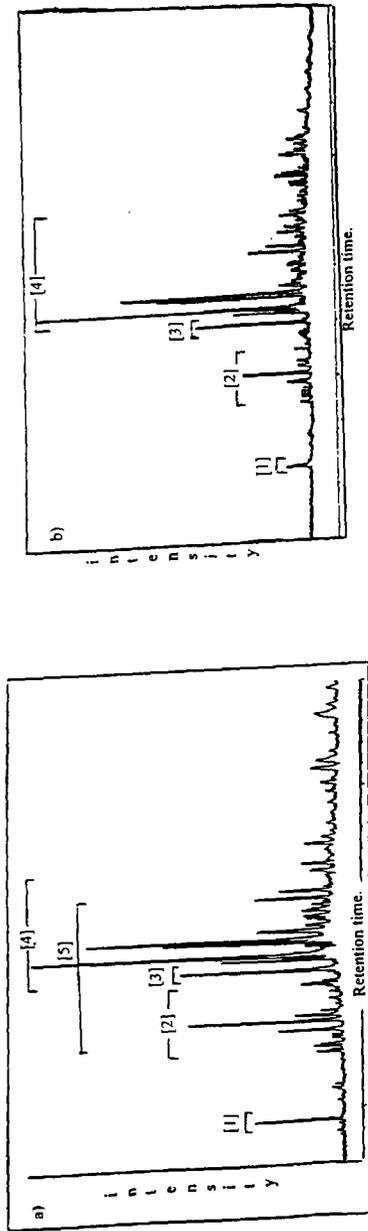


Figure 2. A coal tar pitch (S.P. 1050°C), heat treated at 350°C: a) AED 175nm channel and b) NPD nitrogen response. General assignments: [1] carbazole; [2] substituted carbazoles; [3] benzocridine and [4] benzocarbazoles. [5] See Figure 3b) for an enlargement of this region.

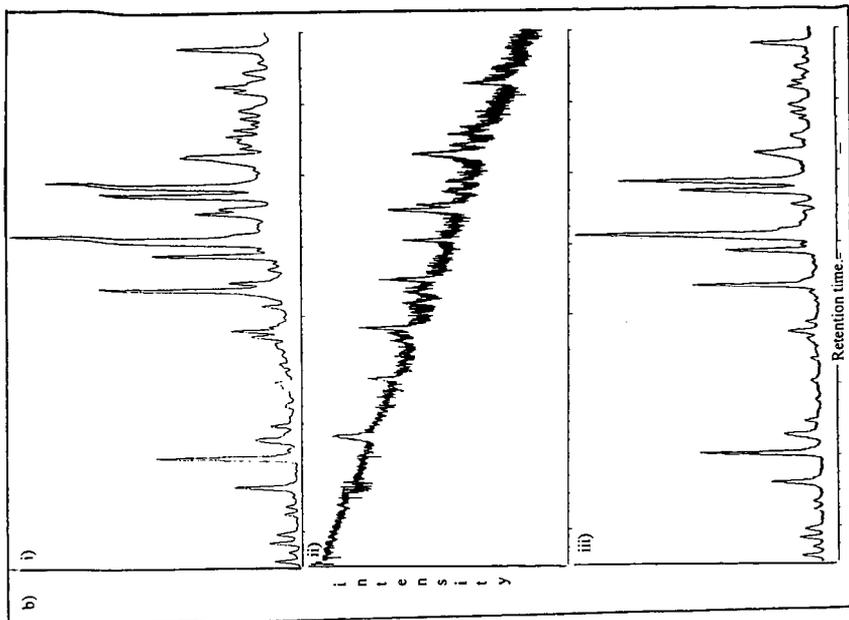
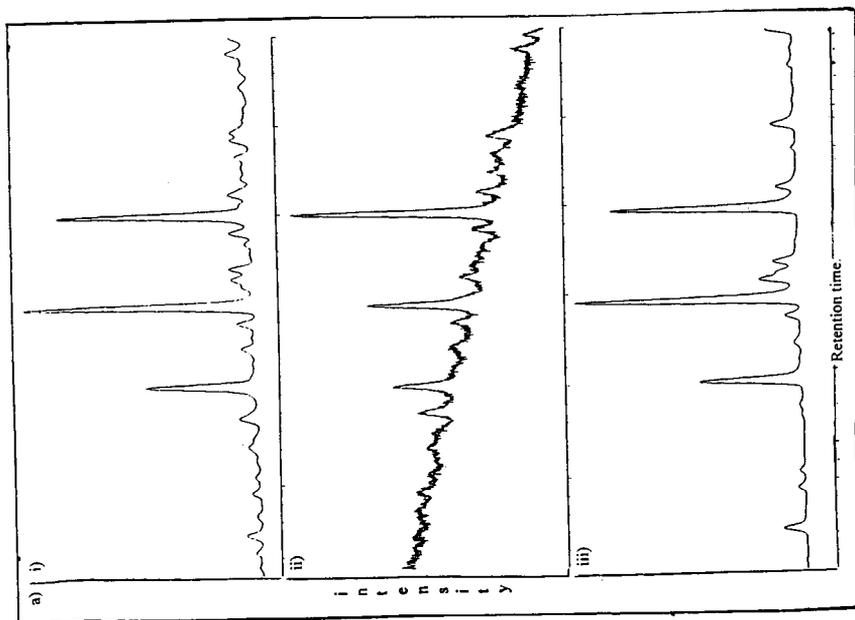


Figure 3. a) A supercritical gas extract of Mequinenza lignite: the GC-AED response on. i) the carbon 193nm channel; ii) the oxygen 777nm channel and iii) the sulphur 181 nm channel.
 b) A coal tar pitch (S.P. 105°C), heat treated at 350°C: the GC-AED response on. i) the carbon 193nm channel; ii) the oxygen 777nm channel and iii) the nitrogen 174nm channel.

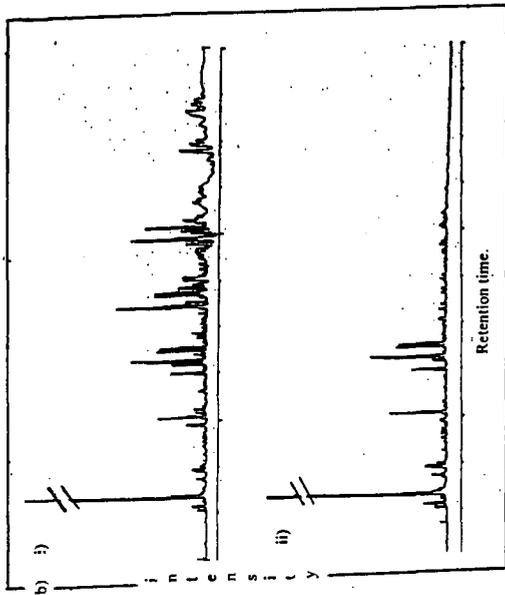
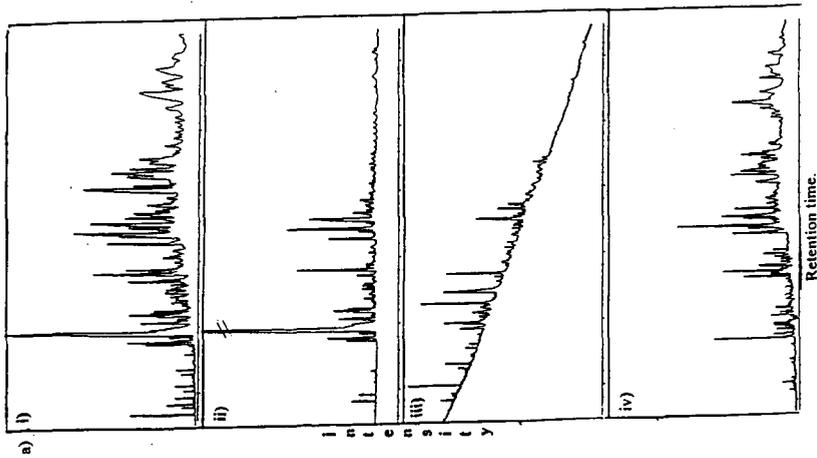


Figure 4. An untreated coal tar pitch (S.P. 35°C): a) the GC-AED response on: i) the carbon 193nm channel; ii) the nitrogen 175nm channel; iii) the oxygen 777nm channel and iv) the sulphur 181 nm channel. b) i) the FID carbon response and ii) the NPD nitrogen response.