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Comprehensive two-dimensional gas chromatography with atomic emission detection and correlation with mass spectrometric detection: principles and application in petrochemical analysis

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Abstract

Comprehensive gas chromatography (GC × GC) has been combined with atomic emission detection (AED) to enable element-selective detection. Under optimised experimental conditions, the requirement of minimum five data points across a peak can be obtained even for analytes eluting early from the second-dimension column. Simple manipulation of the results allows the combined presentation of up to four sets of elemental data in one two-dimensional plot. GC × GC with AED and mass spectrometric (MS) detection in petrochemical analysis for fingerprinting as well as the identification of N- and S-containing unknowns is presented as an application.

Keywords: Gas chromatography, comprehensive two-dimensional; Petrochemical samples; Atomic emission detection; Mass spectrometry; Sulphur heterocyclic compounds

1. Introduction

In the first years after its introduction in the 1990s, comprehensive two-dimensional gas chromatography (GC × GC) was mainly used in petrochemical analysis. More recently, the proven advantages of the technique have sparked interest in many other fields, such as environmental, food and air analysis and, at present, over 100 papers have been published in this area (see, e.g. [1–3]). However, the range of detectors that has been used so far, is limited. One main reason is the small width of the second-dimension chromatographic peaks, which can be as narrow as 100–300 ms at their base. Proper registration—which includes accurate peak apex location, an important issue in the identification process—then requires detectors with small dead volumes and sufficiently high acquisition rates. The obvious early choice was the flame ionisation detector (FID) which operates at frequencies of, typically, 50–200 Hz and, moreover, is the detector in use for most petrochemical analyses. Recently, a miniaturised electron-capture detector, the Agilent μ-ECD, has been shown to be a successful selective detector for the GC × GC analysis of a wide variety of halogenated compounds [4–6]. More importantly, with the introduction of the fast acquiring time-of-flight mass spectrometer (TOF-MS), the possibility of structure-related detection, i.e. identification, has been created [1,7,8].

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In previous work in our group, the use of atomic emission detection (AED) data complementary to mass spectrometric (MS) information for the identification of unknowns was studied in some detail [9,10]. Specifically, such data were found to be highly useful for, on the one hand, confirmation of high-quality mass spectral library hits (elemental composition) and, on the other hand, to act as a powerful aid for the reduction of the number of candidate compounds when the confidence levels of the library hits are low (selective element traces). The individual element traces also yield rewarding results when a general screening for compounds containing a specific element, e.g. Cl or Br, is the main goal of the exploratory study: the subsequent MS analysis can then be targeted very precisely at the 'hot spots'.

Although the resolution of GC × GC is—as experience has meanwhile abundantly demonstrated—much higher than that of conventional one-dimensional GC, the same experience has taught that many separation problems still are not solved at all. In other words, the added potential of AED detection is most welcome. In this paper we explore, for the first time, whether combining GC×GC with, in principle, much too slow AED detection holds any promise for the future. Petrochemical analysis is the application area used for testing.

2. Experimental

2.1. Materials

The pesticide standard was prepared by dissolving analytical-grade pesticides obtained from various sources in ethyl acetate (J.T. Baker, Deventer, The Netherlands). An *n*-alkylbis(trifluoromethyl)-phosphinesulphide mixture (so-called M-series; alkyl: C6, C8, . . . , C18; Nordion, Helsinki, Finland) was added to the pesticide mixture, with a final concentration of 50 ng/μl for all compounds. A crude oil and a fluidised catalyst cracking (FCC) product, sulphur content, 2.3 and 1.8 wt.%, respectively, were a gift from an oil refinery plant.

2.2. Instrumentation and methods

An HP5980/II gas chromatograph equipped with an HP7673 autosampler and an HP5921A atomic emission detector was used for all AED experiments (Hewlett-Packard, Wilmington, DE, USA). The first- and second-dimension columns were a 15 m × 0.25 mm × 0.25 μm J&W DB-1 (Agilent, Amstelveen, The Netherlands) and a 0.6 m × 0.1 mm × 0.1 μm BPX-50 (SGE, Milton Keynes, UK) column, respectively. The second-dimension column was connected to the AED via a 0.7 m × 0.25 mm deactivated fused silica capillary (BGB Analytik, Anwil, Switzerland) kept at 280 °C. The cavity and cooling water were kept at 300 and 60 °C, respectively. The AED helium make-up flow was set at 20 ml/min. Standard wavelengths and reagent gas pressures were used for the three sets of elements: set 1: C 496 nm; H 486 nm; Cl 479 nm; Br 478 nm; set 2: C 193 nm; S 181 nm; N 174 nm; set 3: P 178 nm (also see Section 3).

GC × GC–MS was performed with an HP6890 gas chromatograph and a Leco (Mönchengladbach, Germany) Pegasus II TOF-MS equipped with an electron ionisation (EI) ion source. The multi-channel plate voltage was 1900 V, the EI energy 70 eV, the acquisition rate 50 Hz and the mass range 50–450 amu. The first- and second-dimension columns were the same as used for the AED set-up; however, instead of a deactivated fused silica connection, the final 0.3 m of the 0.9 m second-dimension column was used as transfer line and kept at 280 °C.

For analyte identification, in-house developed software was used which eliminated part of the manual operations earlier required. The MS software that has to be used to record the data, has not been designed to handle GC × GC data; the data are stored linearly in time. Until now, the conversion of the two-dimensional into linear one-dimensional time (s) was performed manually. Next, the experimental spectrum at that time had to be retrieved manually from the MS software. With the new software this procedure is automated: by clicking the peak of interest in the GC × GC chromatogram, the MS software is triggered to display the experimental mass spectrum and the library hit.

In both systems, an in-house constructed dual-stage liquid CO_2 jet modulator was used to modulate the first-dimension column eluent (Fig. 1A). Modulation takes place by immobilising the analytes by a stream of expanding liquid CO_2, and subsequent mobilisation through heating by the hot air of the GC oven when the stream of CO_2 is switched off. The jet on the left-hand side is used to prevent breakthrough of

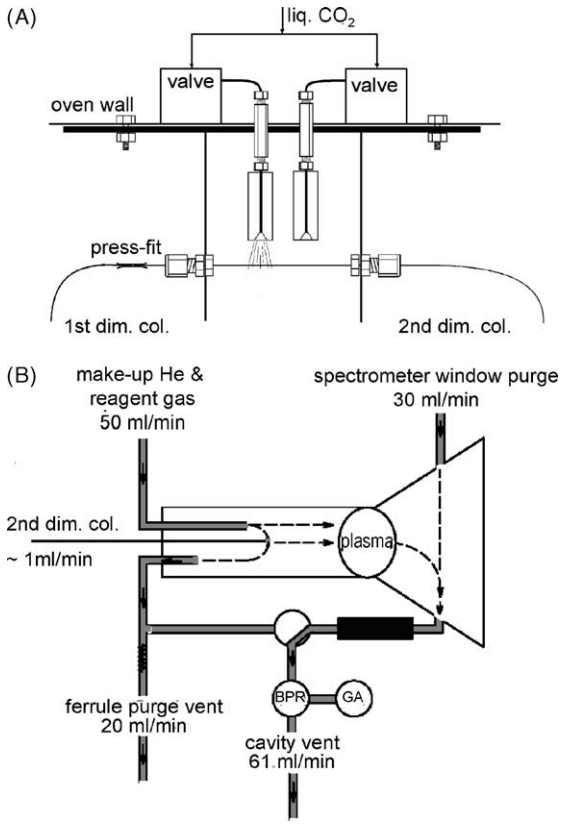

Fig. 1. (A) Dual-stage liquid CO_2 jet modulator. The analytes are immobilised on the head of the second-dimension column which is kept under slight tension by the spring action of the brackets. (B) Schematic showing the gas flows in the AED plasma. Out of the 50 ml/min of helium which is supplied, 20 ml/min is used as plasma make-up gas and 20 ml/min for column venting.

the analytes during the time then the right-hand jet is switched off. The electric valves are actuated by a programmable laboratory-built controller. In all experiments the jets were switched alternately every 4 s. Since the re-injection on the second-dimension column takes place when the right-hand valve is closed, the modulation period is 8 s. Analyte immobilisation occurs in the first part of the second-dimension column. About 5 cm of this column protrudes from the right-hand side of the modulator to allow for easy connection with the first-dimension column; another 5 cm is located within the modulator. Therefore, 0.5 m of the overall 0.6 m second-dimension column located in the oven, is effectively used for separation. For further details, see [11].

Hot-split 1-μl injections were performed at a constant temperature of 260 °C using an Optic II programmable injector with a multi-capillary liner (ATAS, Veldhoven, The Netherlands). The GC columns were operated in the constant-pressure mode using helium (99.999%, Praxair, Oevel, Belgium) at 200 kPa as carrier gas. For the analyses of the pesticides standard a split ratio of 1:50 was used; the oven start temperature was 80 °C (no hold) with a programming rate of 5 °C/min to 280 °C. The petrochemical samples were injected using a split ratio of 1:200; the oven start temperature was 60 °C (no hold) with a subsequent programming rate of 3 °C/min to 280 °C.

3. Results and discussion

3.1. Relevant AED characteristics

The commercial AED uses a 50 W microwave generator and a re-entrant cavity to focus the energy into a 1 mm i.d. fused silica tube in which a plasma is sustained by a steady flow of helium make-up gas. A spectrometer employing a diffraction grating and a movable photodiode array views the plasma axially and can detect the emitted radiation in the 160–800 nm region with a 0.1 nm resolution at 400 nm. However, out of this total range only 20-nm wide segments can be measured during one run (also see Section 3.1.3). For a detailed description, see [12,13].

3.1.1. Dead volume

For a detector to be applicable in GC × GC it has to be capable to record very narrow peaks. The acquisition rate and the detector volume or, when using make-up gases, the effective dead volume, are the key parameters. A GC peak with a width of 300 ms at the baseline, will occupy a volume of approximately 5 μl at a flow rate of 1 ml/min. To avoid undue extra-column peak broadening, the detector volume should be several times smaller than this peak volume. With 12 μl the AED detector volume is much too large, were it not for the make-up gas flow that is necessary to maintain a stable plasma.

In the HP5921A the plasma is completely enclosed (Fig. 1B), which prevents atmospheric back-diffusion

into the plasma. This permits stable plasma operation at helium flows as low as 5 ml/min. However, in experimental practice a make-up flow of about 30 ml/min is used to prevent excessive peak tailing caused by reactions of the ionised analyte products on the discharge tube wall and/or dead-volume effects [12]. Another factor that seriously reduces the effective dead volume is the column venting system (Fig. 1B) which consists of a continuous flow of helium at 20 ml/min that purges the area around the GC column outlet.

To contrast the impression that the use of a higher make-up gas flow is purely beneficial, one should realise that (i) the analytes are diluted by the make-up gas and (ii) the higher linear speed reduces the residence time in the plasma. As a consequence, the analyte detectability is adversely affected and an optimum has to be selected depending on the type of application. For example, when there is no sample-size limitation the amount introduced onto the column can be increased (lower split ratio or larger injection volume) and the make-up flow increased to avoid peak broadening due to dead volume. However, this scenario only holds fully true when the acquisition rate is no limitation.

3.1.2. Acquisition rate

The GC peaks should be wide enough to allow a sufficient number of sampling periods at the maximum acquisition rate of the AED, which is 10 scans/s. Although the minimum number of data points across a peak is three for a triangular peak—not really considered good chromatographic practice, but acceptable for qualitative analysis—at least five data points are required for an adequate description and the elimination of noise and spiking problems. With this minimum requirement, the peak width at the base should cover at least four sampling periods. For an acquisition rate of 10 Hz, this means that the peaks should have a baseline width of at least 400 ms. In other words, for peaks that can be as narrow as 100–300 ms when using GC × GC under optimal conditions, some (intended) broadening may be required for proper registration using the AED. Actually, the transfer line that connects the GC and the AED may be of some ‘help’ here in that it will cause some peak broadening. To enhance the effect, a 0.25 mm instead of a 0.1 mm i.d. transfer line was used.

Peak widths also depend on the second-dimension retention time. Although temperature programming is used and the first- and second-dimension columns are immersed in the same oven, the change in temperature during the very fast separations on the second-dimension column is so small that these separations can be regarded as isothermal. As a consequence, peaks eluting early in the second dimension are the narrowest ones. Experience showed that under the experimental conditions used in this study, such peaks typically had a baseline width of approximately 500 ms (with some broadening caused by minor tailing): that is, six data points could be used to describe the peak. In other words, the limited, but more or less deliberately introduced additional band broadening compared with GC × GC–FID (where values of about 150 ms have been reported [11]) has created conditions which allow the AED to be used as a detector for GC × GC.

3.1.3. Data recording and presentation

A phenomenon that complicates the use of AED detection in conventional one-dimensional GC as well as GC × GC is that several runs are required to unravel the elemental composition of the analyte of interest. This is caused by the fact that (i) a very high resolution is required and (ii) the plasma has to be doped with reagent gases to increase selectivity and prevent peak tailing for some specific elements. Briefly, to enable the simultaneous recording of several wavelengths, a photo diode array (PDA) is used which, in the HP5921A, is a 12-mm long array with 211 diodes. The instrument has been designed to provide 0.1 mm resolution at 400 nm, which implies that a window of 211 × 0.1 or 20 nm is spanned by the PDA. Actually, depending on the position in the 160–800 nm focal plane, the window varies between 10 and 30 nm. Most importantly, simultaneous measurement of several elements is possible only when their emission lines are within the same window [13,14].

As regards doping of the plasma, a few examples may serve to illustrate the problems. Elements which form refractory oxides such as phosphorus or boron require hydrogen, while oxygen has to be used when carbon, hydrogen, chlorine and bromine are determined. In addition, even with hydrogen as a reagent gas, the phosphorus trace shows extensive tailing unless a very

Table 1
Test analytes used in the study and their second-dimension retention times

Analyte	Formula	Second-dimension retention time (s)					
		C	Cl	Br	N	S	P
M1	$C_6H_{13}PS(CF_3)_2$	0.53				0.62	0.63
M2	$C_8H_{17}PS(CF_3)_2$	0.55				0.70	0.51
M3	$C_{10}H_{21}PS(CF_3)_2$	0.62				0.62	0.62
M4	$C_{12}H_{25}PS(CF_3)_2$	0.55				0.66	0.58
M5	$C_{14}H_{29}PS(CF_3)_2$	0.60				0.64	0.62
M6	$C_{16}H_{33}PS(CF_3)_2$	0.57				0.66	0.59
M7	$C_{18}H_{37}PS(CF_3)_2$	0.67				0.69	0.65
P1 Diazinon	$C_{12}H_{21}N_2O_3PS$	1.96			2.05	1.99	1.94
P2 Fenchlorphos	$C_8H_8Cl_3O_3PS$	2.25	2.29			2.29	2.21
P3 Fenitrothion	$C_9H_{12}NO_5PS$	2.96			2.98	2.99	2.92
p4 Malathion	$C_{10}H_{19}O_6PS_2$	2.67				2.69	2.65
P5 Chlorpyrifos	$C_9H_{11}C_{l3}NO_3PS$	2.26	2.28		2.26	2.24	2.21
P6 Bromophos	$C_8H_8BrCl_2O_3PS$	2.46	2.48	2.47		2.54	2.46
P7 Bromophos-ethyl	$C_{10}H_{12}BrCl_2O_3PS$	2.14	2.20	2.20		2.16	2.05
P8 Azinphos-methyl	$C_{10}H_{12}N_3O_3PS_2$	4.94			5.07	5.10	4.98
P9 Pyrazophos	$C_{14}H_{20}N_3O_5PS$	3.08			3.21	3.20	
P10 Coumaphos	$C_{14}H_{16}ClO_5PS$	3.68	3.76			3.75	3.62

high make-up flow of 180, instead of the conventional 30 ml/min is used.

For the pesticide analysis, three runs were performed to record the C, H, Cl, Br, S, N and P traces. Each run included at least one element which enabled the detection of the marker compounds, i.e. the M-series, viz. C for set 1, S for set 2 and P for set 3. Typical results are presented in Table 1. These are highly encouraging as regards the most critical parameter to be studied when combining data from several runs is an issue, viz. mutual differences in second-dimension retention times. The differences are seen to be small, i.e. 0.05–0.10 s in most cases, with a few exceptions of 0.10–0.15 s. Similar results were reported in a study on pesticides, where differences of 0.01–0.20 s were found for a large majority of all analytes [15]. One should add that repeatability data in another study [16] indicate that further improvement should be possible.

A colour-plot presentation for four elements is given in Fig. 2. Since all the M-series compounds all exhibit closely similar second-dimension retention times—because identical functional groups, but not the alkyl chains determine the interaction—the marker spots show up at regular intervals in the lower part of the 2D plots and can be used for unambiguous alignment of various GC × GC–AED runs. Of course, a distinct disadvantage of the presentation of separate plots is that, with more complex samples, it becomes increasingly difficult to rapidly discern the combination of elements that is present in a specific analyte of interest. Fig. 3 illustrates how a much improved result can be obtained by means of a procedure which requires little data processing. For this figure, the colour plots of the various elements were overlaid while using a slight offset in the direction of the *Y* axis. Obviously, when adequate enlargement is used and three to four element traces are combined per frame, a fully satisfactory result is obtained and the (qualitative) element composition of each analyte can immediately be read from the spot colours.

3.2. Application: petrochemical analysis

Desulphurisation of fuels receives much attention today because of the urgent need to reduce the adverse effects of fuel combustion on the environment. The development of novel catalysts requires detailed knowledge of the molecular structures of the sulphur-containing compounds present in crude oil and intermediate products. The detectors of first choice for such analyses are selective detectors such

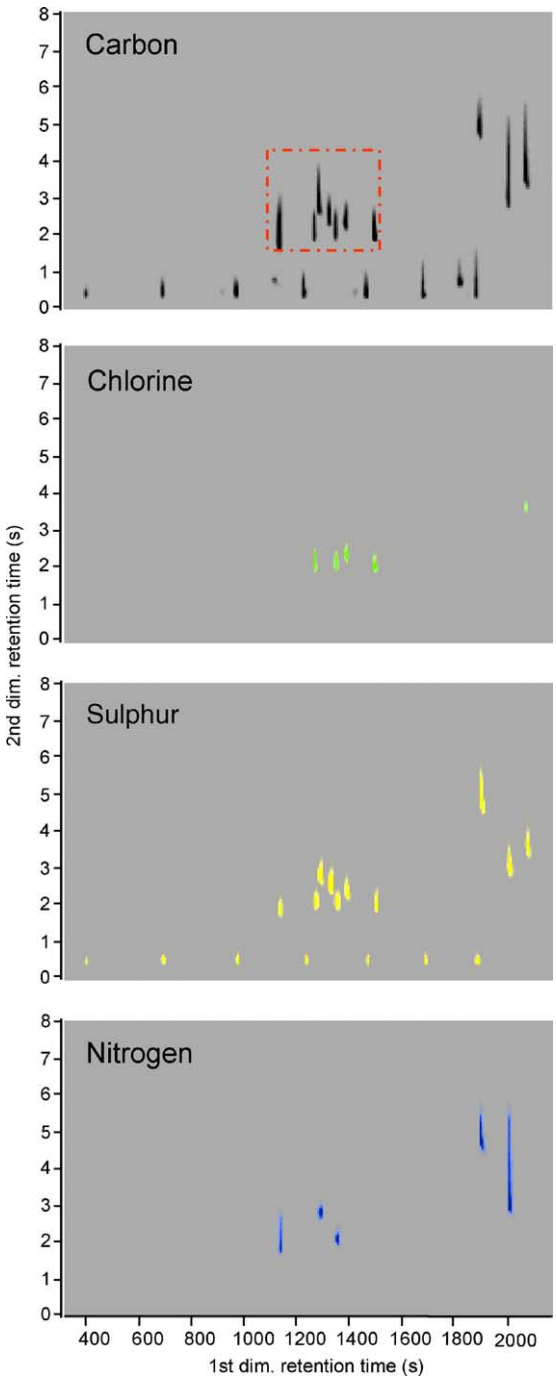

Fig. 2. GC × GC–AED of mixture of pesticides and marker compounds; the latter show up at second-dimension retention times of about 0.5 s. For red rectangle in carbon frame, see Fig. 3.

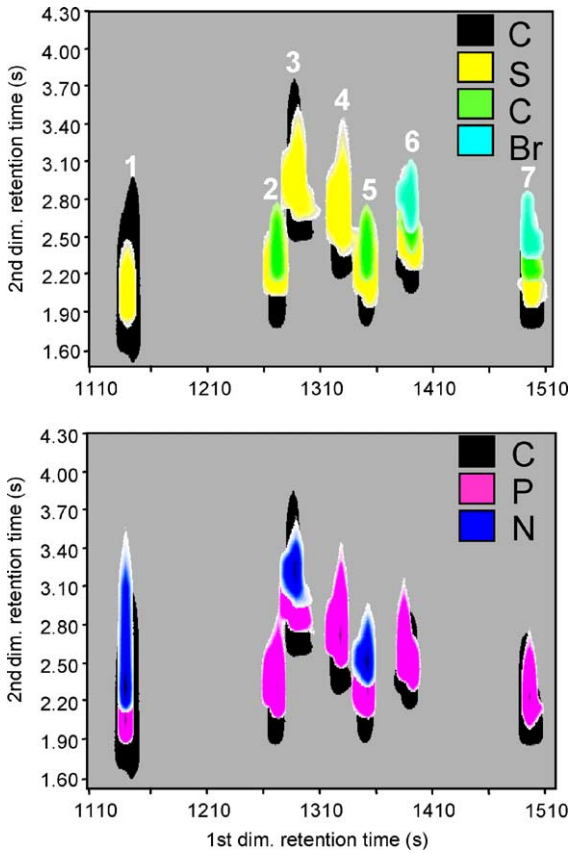

Fig. 3. Combined presentation of elemental composition data of pesticides present in red rectangle indicated in Fig. 2. Slight shifts of every 'element layer' in *Y* axis direction prevent loss of visual information. For peak identification, see P1–P7 in Table 1.

as the sulphur chemiluminescence detector (SCD), the pulsed flame photometric detector (PFPD) and the AED. These detectors all show limits of detection (LOD) of 0.5–2 pg S/s [17]. With one-dimensional GC, such selective screening provides a rapid provisional classification of the main S-containing compounds present in a sample. However, as is vividly illustrated in, e.g. a study by Amorelli et al. [18] on the use of GC–AED, there is a serious overlap of the several analyte classes of interest (Fig. 6 of that study). Improved performance requires the use of extensive and time-consuming sample work-up and/or fractionation (see, e.g. [19–21]) or hyphenated analyses [22] which is not really attractive. In other words, another solution is of distinct interest.

To investigate the practicality of GC × GC–AED to separate the main classes of S-containing compounds—aliphatic and aromatic thiols, alkylated benzothiophenes (BTs), dibenzothiophenes (DBTs) and benzonaphthothiophenes (BNTs)—a crude oil and a fluidised catalytic cracking (FCC) product were analysed. Next to lower-boiling compounds, a crude oil contains high-boiling alkanes and heavily alkylated ring structures which, depending on the source, may be dominant. FCC is used to convert long (>C12) into shorter (<C5) alkyl chains to produce lighter fuels. Fig. 4 shows two typical GC × GC–AED

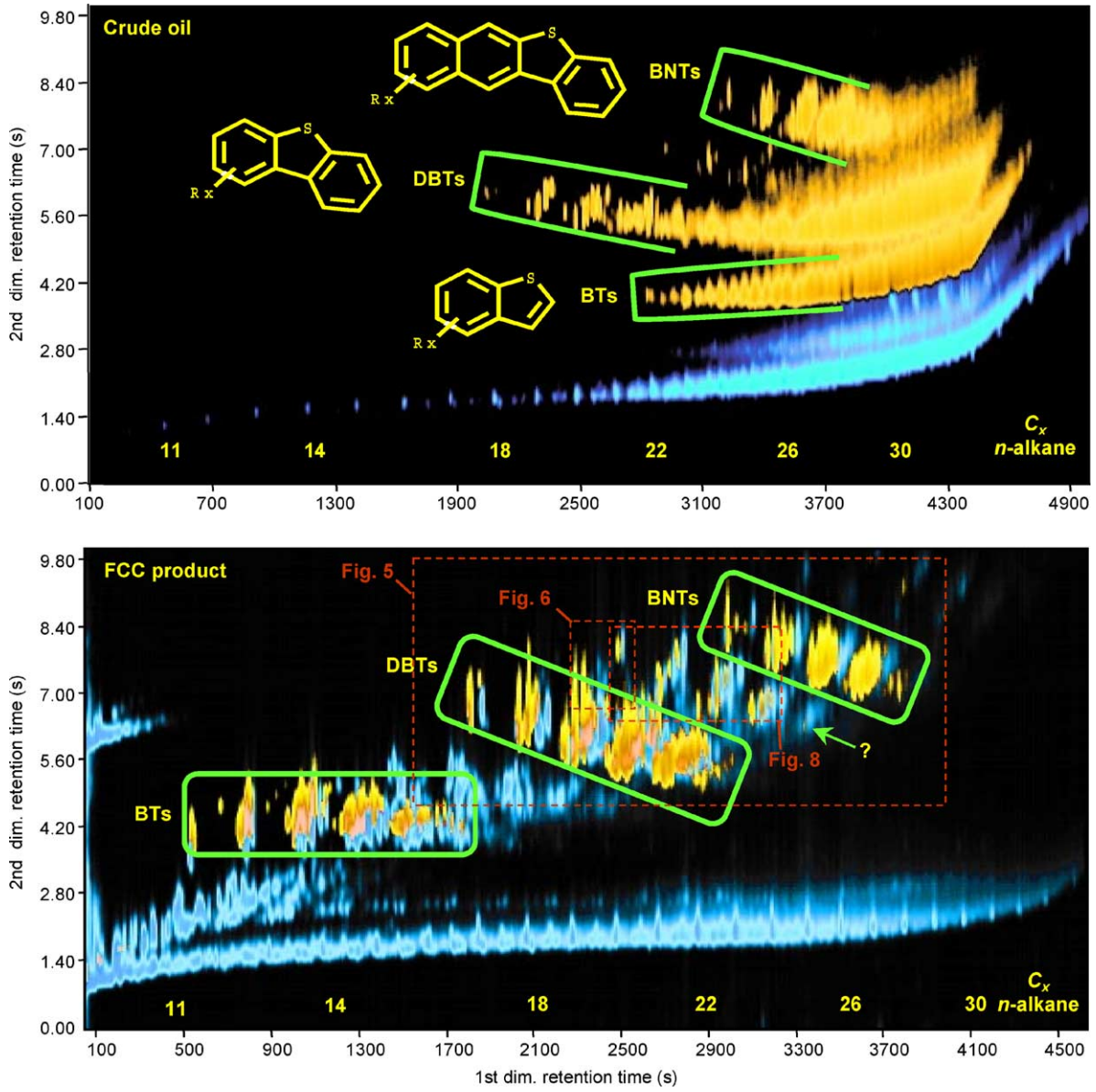

Fig. 4. GC × GC–AED of a crude oil (top) and an FCC product (bottom). The sulphur (orange) and carbon (blue) channels are indicated. For further explanation, see text.

chromatograms over the entire elution temperature range which was covered, with both the carbon (blue) and the sulphur (orange) channels being displayed. When focusing attention on the latter signal of the crude oil, one mainly sees heavily alkylated BTs, DBTs and BNTs, which are visible as continuous bands with their intensity increasing at higher retention times. In the FCC product, however, the high-boiling sulphur compounds are absent and moderately alkylated (C_1–C_6) aromatic sulphur compounds dominate. The widely different carbon profiles illustrate the effect of the FCC conversion to short carbon chains. One group of sulphur-containing compounds of interest are those situated between the DBTs and BNTs, which are indicated by a question mark because they do not belong to any of the aforementioned groups. These compounds were also detected, but not identified, in a GC × GC–SCD study by Wang et al. [23].

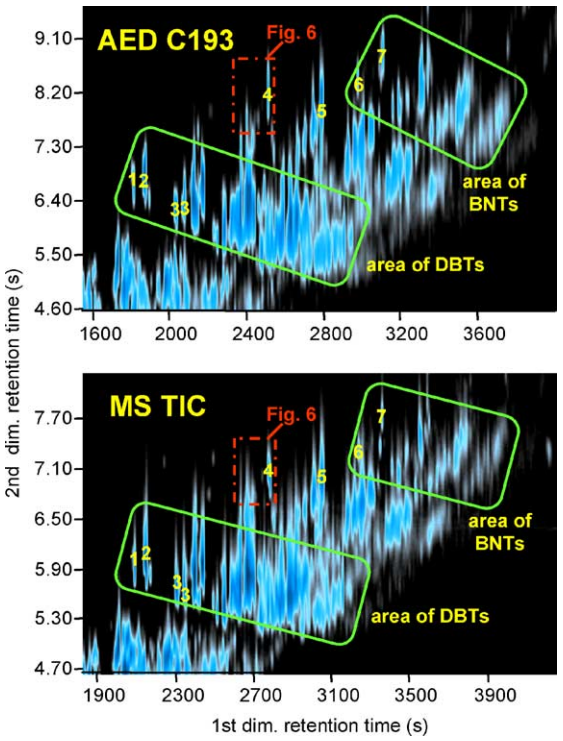

Fig. 5. Retention time correlation between AED C channel (top) and TIC MS chromatogram (bottom) by stretching-plus-shifting and modulation-time manipulation. Marker compounds indicated: 1, DBT; 2, phenanthrene; 3, Me-DBT; 4, pyrene; 5, Me-pyrene; 6, BNT; 7, chrysene.

Further study of a class of unknowns as mentioned in the previous paragraph requires the combined, and correlated, use of AED and MS detection. The main difficulty of correlating the two sets of data is the difference in column outlet pressure, with the MS being held at vacuum and the AED at near-atmospheric pressure. As the inlet pressure was the same in both systems, the pressure at the point of connection of the two columns is different; hence, the first- and second-dimension retention times are affected. Consequently, straightforward correlation is not possible.

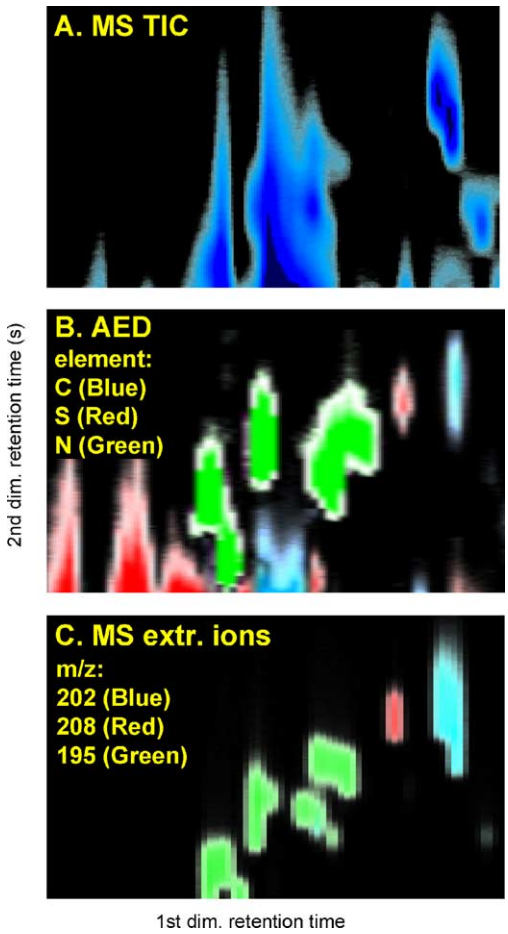

Fig. 6. Correlation and identification of compounds in selected part (see rectangle indicated in Fig. 5) of the FCC product. The AED signals (B) were used to locate the compounds in the TIC MS chromatogram (A). Extracted ion traces (C) were then constituted, viz. for dimethylcarbazoles (*m*/*z* 195) and pyrene (*m*/*z* 202) and, tentatively phenanthro[4,5-bcd]thiophene (*m*/*z* 208). For details, see text.

A solution was found by shifting and stretching one of the chromatograms along the first-dimension axis, and by also changing the modulation time used for converting the one-dimensional chromatogram into a two-dimensional plot. Although the modulation time actually used during the GC × GC analysis is constant, the modulation time used for graphical conversion can be varied. This causes a change of angle relative to the *X* axis. After such manipulation had been successfully performed for the carbon channel of the AED and the MS total ion chromatogram (TIC)—as is demonstrated in Fig. 5, where several marker compounds are indicated—the same parameters were used to convert other AED channels and extracted ion chromatograms.

As nitrogen can be monitored under the same conditions (i.e. in the same run) as sulphur, this channel was also recorded. Although the number of nitrogen-containing compounds that was detected, was only about 10, they form an interesting group for a first test of the AED versus MS correlation. This is because compounds containing an uneven number of nitrogen atoms have an uneven molecular mass and therefore show a rather 'unique' mass spectrum amongst most other compounds which possess even molecular masses. Some of these nitrogen compounds elute in the same region as do the unknown sulphur compounds mentioned before. The rather blurred TIC MS chromatogram displayed in Fig. 6A clearly reveals that a search for unknowns indeed requires the targeted information on individual elements shown in Fig. 6B. In-house developed software, in which several steps of the earlier, manual [15], procedure had been automated (cf. Section 2) was used for the subsequent identification.

All N-containing compounds in the area shown in Fig. 6B turned out to be dimethylcarbazoles. One example is shown in Fig. 7A; similarly high match factors as indicated here (*m*/*z* 914) were found for the other compounds. As a further confirmation of identity, manual checking showed a good mutual match of the peak shapes of the relevant individual ion traces.

The S-containing compound of interest in the two-dimensional plane of Fig. 6B is the red-coloured spot in the top right-hand corner of the AED chromatogram; its base peak was at *m*/*z* 208. To emphasise the need for proper alignment, it is interesting to note that, prior to this procedure, the peak was erroneously identified as 1,8-anthracenediamine (*m*/*z* 208, but no sulphur and incorrect fragment ions; similarity 610). After alignment, additional information was derived from the elution of pyrene ($C_{16}H_{10}$; *m*/*z* 202; blue spot in Fig. 6C) in the close two-dimensional

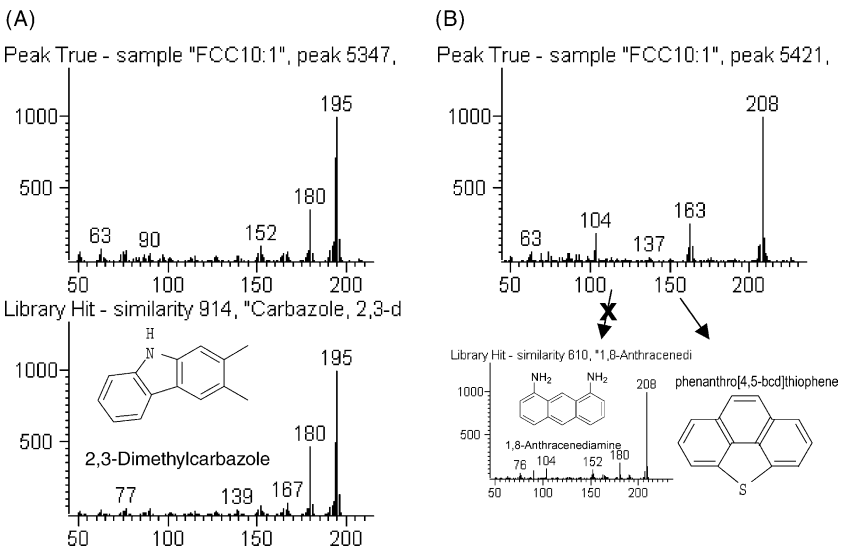

Fig. 7. (A) Mass spectrum of one of the nitrogen peaks in Fig. 6, and corresponding library spectrum. (B) Mass spectrum of S-containing peak in Fig. 6. Initial identification had poor fit. For explanation of subsequently proposed structure, see text.

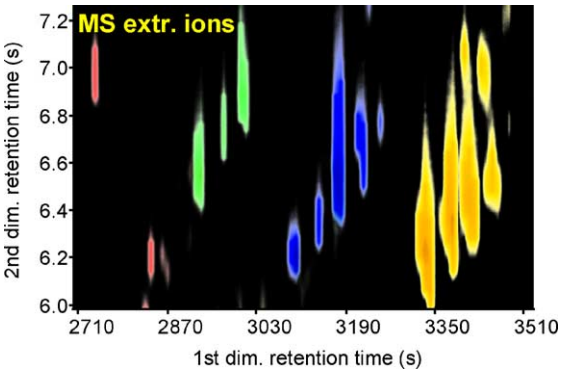

Fig. 8. GC × GC–MS extracted ion chromatogram of FCC product. Traces shown are *m*/*z* 208 (red), with the spot in the upper left-hand corner being the tentatively identified phenanthro[4,5-bcd]thiophene, and the alkylated congeners *m*/*z* 222 (green), *m*/*z* 236 (blue) and *m*/*z* 250 (yellow). The corresponding area in the GC × GC–AED chromatogram is indicated in Fig. 4.

vicinity of the S-containing unknown, which suggests similar aromaticity. On the basis of the combined information now available, the number of molecular formulae could be drastically limited, with unsaturated $C_{14}H_8S$ compounds as the most likely candidates. To all probability the analyte of interest is phenanthro[4,5-bcd]thiophene (Fig. 7B). The *m*/*z* 163 ion indicates the loss of CHS^+ (45 amu) which confirms the presence of sulphur, while the doubly charged ion (at *m*/*z* 104) is typical for aromatic compounds. Since phenanthro[4,5-bcd]thiophene is not commonly reported in oil fractions, a literature study was performed to substantiate the identification. The non-alkylated and methylated analogues were found in coal liquids and shale oils [20,24] and in the workplace air of an aluminium melting plant [25], up to C3-alkylated compounds in coal [26], and up to C7-alkylated congeners in vacuum gas oil [21]. Finally, extracted ion GC × GC chromatograms of masses associated with the alkylated forms of phenanthro[4,5-bcd]thiophene such as *m*/*z* 222, 236 and 250 revealed that these compounds are also present in the samples analysed in this study. This is demonstrated in Fig. 8.

4. Conclusions

GC × GC can be on-line combined with AED detection to provide valuable element-selective information. Minor adaptations of the transfer line dimensions and the gas flow rates, and the use of the highest acquisition rate available (10 Hz) suffice to record at least five or six data points even for peaks rapidly eluting from the second-dimension column. The use of 'element overlays' allows an easy screening for compounds featuring specific combinations of elements. Combination of GC × GC–AED and GC × GC–TOF-MS information is highly useful when screening for selected types, e.g. S-containing of unknowns. Ordered structures, which typically indicate the presence of sets of related compounds, considerably help to solve identification problems. More sophisticated studies, with higher AED/MS correlation, will be possible by using a precisely 'tuned' restriction capillary in front of the MS inlet or by including both detectors in one GC × GC set-up.

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