Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1050 (2004) 77–84
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Comprehensive two-dimensional gas chromatography coupled with fast sulphur-chemiluminescence detection: implications of detector electronics

Jan Blomberg*, Toby Riemersma, Manfred van Zuijlen, Hassan Chaabani

Shell International Chemicals B.V., Shell Research and Technology Centre, Badhuisweg 3, 1031 CM, Amsterdam, The Netherlands

A large part of this manuscript is based on the bachelor thesis of Toby Riemersma. Unfortunately, Toby did not live to see the publication of his work. After a courageous but unequal fight of somewhat less than a year, Toby was taken away from us the 21st of May 2004. We will miss his enthusiasm and dedication he showed towards chemistry, but mostly towards life.

Abstract

Within the petrochemical industry, there has been a growing interest in methods capable of providing detailed information on the distribution of sulphur-containing compounds in various product streams, going down to the level of separating and quantifying individual sulphur species. Since no single capillary gas chromatographic column is able to perform this separation, a refuge to multi-dimensional separation techniques has to be taken. In this respect, comprehensive two-dimensional gas chromatography (GC × GC) coupled with sulphur chemiluminescence detection (SCD) has shown to be highly promising. It has been suggested, however, that the detector volume of an SCD restricts its potential to keep up with the fast second-dimension separations of contemporary GC × GC. In this paper, we will demonstrate that the lack of speed of the SCD does not originate from its physical dimensions, but is largely determined by the speed of the electronics used. Additionally, some typical examples will be presented to illustrate the potential of GC × GC coupled with fast SCD.

Keywords: Gas chromatography, comprehensive two-dimensional; Sulphur chemiluminescence detection; Sulphur-containing compounds

1. Introduction

All petroleum samples, whether this concerns crude oil or refined products, contain varying amounts of components containing heteroatoms. Of these, sulphur and nitrogen are the most predominant. Depending on the origin, crude oil contains sulphur in between 0, 5 and 140 g/kg [1]. The burning of petroleum products containing sulphur will lead to the formation of SO_2.

Since this is an important source of air pollution and acid rain, many countries have implemented strict regulations on sulphur content in gasoline and diesel oil. Besides this air quality related driver, exhaust gas after treatment systems also demand low levels of certain elements and components in the fuel in order to prevent catalyst poisoning. Therefore, changes to fuel specifications have also been and are increasingly driven by the automotive industry, which demands improved fuel quality to assist in meeting the very tough new exhaust emissions legislations. Moreover, if gasoline is to be used as a fuel for fuel cell reformers, S levels down to 1–2 mg/kg may even be required.

A number of laboratory methods for total-sulphur measurements with ASTM, IP or other approval are available that suffice for legislation purposes. Of these, combustion/ultraviolet fluorescence (UVF)[1] and wavelength dispersive X-ray fluorescence spectrometry (WD-XRF)[2] are gaining popularity.

Some sort of sulphur speciation, however, is often required in addition to the determination of the total amount of sulphur. Different groups of sulphur-containing compounds

* Corresponding author. Tel.: +31 20 630 3568; fax: +31 20 630 2911.
E-mail address: jan.blomberg@Shell.com (J. Blomberg).

[1] ASTM D5453-93 Standard test method for the determination of total sulphur in light hydrocarbons, motor fuels and oils by ultraviolet fluorescence.

[2] ASTM D2622-98 Standard test method for sulphur in petroleum products by wavelength dispersive X-ray fluorescence spectrometry.

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.07.105

generally show a different behaviour with respect to catalyst poisoning, equipment corrosion and sulphur-removal processes such as hydrodesulphurisation (HDS). Therefore, an array of sulphur-selective detectors for chromatography has been developed for the analysis of organo-sulphur compounds in petroleum products, the pulsed flame-photometric detector [2] being the most recent development.

Several investigators have reported on the chemistry and kinetics in HDS [3–7]. Generally speaking, in HDS the reactivity of sulphur-containing compounds in *middle-distillates* (kerosene, diesel, boiling-range 150–450 °C), decreases strongly in the series thiols > sulphides > thiophenes > benzothiophenes > dibenzothiophenes [3,7]. Even the reactivity of individual sulphur-species within a group can vary. Reactivity of benzothiophene, for instance, is lowered significantly by substitution especially in the 3-position and less in the 7-position [3]. Methyl substituents in the 4- and 4,6-positions (but not in the other positions) significantly reduce the reactivity of dibenzothiophenes, which can be explained by mild steric effects [6]. It is for this reason that not merely the various sulphur-containing groups present, but also those species particularly refractory to HDS have to be separated and quantified. Since no single capillary GC column is able to perform this separation, a refuge to multi-dimensional separation techniques has to be taken. Beens and Tijssen [8] were the first to accommodate for this need when they reported on their on-line coupling of a sulphur group-type separation by NPLC with the high-resolution of GC. This approach, although very elegant and meeting the requirements delineated above, has never gained wide acceptance, probably due to instrumental complexity and required operator skills.

In this respect, comprehensive two-dimensional gas chromatography (GC × GC) coupled with sulphur-selective detection, especially when utilized with the recent instrumental improvements, proves to be a viable alternative. The recent developments in cryogenic modulation have resulted in simple and robust approaches to enable thermal modulation. Various groups have recognized this alternative. Van Deursen [9] and Dallüge et al. [10] have reported on sulphur speciation by GC × GC coupled with time-of-flight mass-spectrometry (GC × GC-ToF-MS). With a ToF-MS, ion chromatograms can be used to selectively extract groups of compounds on the basis of their unique masses. ToF-MS also enables fast group-type identifications, making it an ideal tool for method development.

For quantification purposes, however, a true sulphur-selective detector with an equimolar response and, preferably, a high selectivity over carbon, is to be preferred. Surprisingly, the atomic-emission detector (AED), although limited in its selectivity over carbon, has been demonstrated to be highly promising [11]. It is doubtful, however, if the latter is capable of revealing the presence of sulphur species at the low levels currently of interest in the studies of desulphurisation processes. Furthermore, the currently commercially available AEDs lack the speed necessary to keep pace with the fast second-dimension separations of contemporary GC × GC set-ups.

The same goes for the P-FPD [2]. Although this detector shows excellent selectivity over carbon, equimolar response and high sensitivity, its physical design limits its sampling frequency to 4–5 Hz.

Currently, the sulphur chemiluminescence detector (SCD) is the only realistic detector of choice for the current demands set. Two groups have already reported on GC × GC coupled with SCD [12,13]. Both groups have observed relatively broad sulphur peaks, which, suggests that the response characteristics of the SCD differ significantly from that of the flame-ionization detector (FID) commonly used in petrochemical applications. Although in the study of Wang et al. [12] this might be caused by the relatively large diameter second-dimension column (3 m × 0.25 mm i.d. bpX-50 Df 0.25 μm), Hua et al. [13] unjustly attribute this to the larger cell volume of the SCD. In this paper, we will demonstrate that the lack of speed of the SCD does not originate from its physical dimensions, but is largely determined by the speed of the electronics used. Additionally, some typical examples will be presented to illustrate the potential of fast SCD.

2. Experimental

2.1. Instrumentation

The gas chromatograph used throughout this study was a Hewlett-Packard 6890 Series GC (Hewlett-Packard, Waldbron, Germany), equipped with an OPTIC I programmable temperature vaporizer (PTV; Ai Cambridge, Cambridge, UK), an FID and a SCD equipped with a ceramic (flameless) burner (Sievers Model 350 sulphur chemiluminescence detector; Sievers, Boulder, CO, USA). For the amplification of the SCD's PMT-signal, a modified FPD electrometer (Carlo Erba FPD-500 electrometer, Carlo Erba Strumentatione, Rodano, Milan, Italy) was used.

For the initial optimisation of the SCD (linear GC experiments), a single 10 m × 0.1 mm i.d., 5% phenyl-methylpolysiloxane column (DB-5, J&W Scientific, Folsom, CA, USA) with a 0.1 mm film was used.

In this study, two types of thermal modulators were used. Initial experiments (see Section 3.1) involved a ZOEX KT2000 retrofit kit (ZOEX Corp., Lincoln, NE, USA). This was the second prototype built of the first generation so-called sweeper modulators [14]. In this set-up, a 10 m × 0.25 mm i.d., dimethylpolysiloxane column (DB-1, J&W Scientific) with 0.25 mm film thickness served as first dimension. The second dimension consisted of a 17.5 cm × 0.10 mm i.d., 50% phenyl (equiv.) polysilphenylene-siloxane column (BPX50, SGE, Ringwood, Vic., Australia) with 0.05 mm film thickness. In between the first- and second-dimension column a piece of 0.09 m × 0.10 mm i.d., 5% phenyl, 1% vinyl-methyl-polysiloxane column (SE-54, Quadrex, New Haven, CT, USA) with a 3 mm film served as modulation capillary.

The second part of the study (see Sections 3.2 and 3.3) employed a ZOEX KT2002 LN_2 Loop modulator with pulsed hot jet (ZOEX Corp., Lincoln, NE, USA). The columns used in this second part of the study were similar to that of the initial experiments, except for the length of the second dimension column. The loop-modulator set-up was equipped with a separate secondary oven with independent temperature control, allowing for a 2 m long second-dimension column to be used. The OPTIC I PTV was replaced by a JAS UNIS 2100 PTV fitted with a JAS 76200 extended heater (Joint Analytical Systems GmbH, Moers, Germany) for its superior ability to effectuate selective discrimination.

The data-acquisition was handled by an EZChrom *Elite* Client/Server data system, Version 2.61 (Scientific Software Inc., Pleasanton, CA, USA). Further data handling was performed with software written in MatLab R13 (The Mathworks, Natick, MA, USA). Data-handling routines were developed in-house [15]. The contour plots in this paper were generated using Transform 3.4 (Noesys, Research Systems, Boulder, CO, USA).

2.2. Materials and standards

The light catalytically cracked cycle oil (LCCCO)–heavy gas oil (HGO) mixture, the Liverpool Bay Crude and the desulphurized samples used in this study, all originate from the Shell Research and Technology Centre, Amsterdam. The dibenzothiophene used in the linear GC experiments and the 2-(3-thienyl) ethanol used as internal standard in the GC × GC analyses had purities of 99% and were obtained from Aldrich (Milwaukee, WI, USA). The 4,6-dimethyldibenzothiophene used for identification purposes had a purity of 97% and was also obtained from Aldrich.

The helium and hydrogen used throughout the experiments both had a quality of (at least) 6.0. Zero-air was supplied by a Parker–Balston zero-air generator (Parker Hannifin Corporation, Tewksbury, MA, USA).

2.3. Conditions

In the linear GC-experiments, 1 μL aliquots of 8.8 mg/kg sulphur (as dibenzothiophene) in xylene were injected. To allow for a rapid release from the PTV injector, the latter had an initial temperature of 300 °C. Immediately after injection, the PTV was heated to 350 °C at a rate of 16 °C/s followed by a 5 min hold. The column head pressure was 250 kPa, and a splitflow of 100 ml/min was used. The oven had an initial temperature of 200 °C. After an initial hold of 1 min, the oven was programmed at a rate of 75 °C/min to 250 °C, which was maintained for 5 min.

In the GC × GC experiments with the sweeper modulator, 0.2 μL aliquots of a high-sulphur kerosene sample were injected. The PTV initial temperature was 40 °C. After injection, the PTV was heated at a rate of 16 °C/s to 350 °C, which was maintained for 5 min. The column head pressure was 100 kPa, and a splitflow of 50 ml/min was used. The entire GC × GC column assembly was located in one oven, which had an initial temperature of 35 °C. After an initial hold of 5 min, the oven temperature was programmed at a rate of 2 °C/min to 300 °C, which was maintained for 5 min. The sweeper-modulator was operated at a temperature of 100 °C above the oven temperature. The stroke velocity was 0.25 rev/s and the pause time 0.5 s. The modulation-period was 7.5 s.

In the GC × GC experiments performed with the loop modulator, 1 μL aliquots of the samples were injected. The JAS UNIS PTV initial temperature was 40 °C. After injection, the PTV was heated at a rate of 12 °C/s to 300 °C, which was maintained for 2 min. Then the temperature of the PTV was forced down to 125 °C in order to prevent the introduction of high-boiling material >*n*-C_{30} through selective exclusion [16], thus protecting the column-set from contamination. This allowed a crude-oil sample to be introduced through neat injection. The column head pressure was 150 kPa, and a splitflow of 20 ml/min was used. The initial oven temperature for the first dimension column was 40 °C. After an initial hold of 5 min, the oven was programmed at a rate of 2 °C/min to 320 °C, which was maintained for 20 min. The secondary oven chamber holding the second dimension column had an initial temperature of 90 °C. After an initial hold of 5 min, it was programmed at a rate of 2 °C/min up to 350 °C, which was maintained for 30 min. The hot-pulse of the loop modulator was programmed with an offset of 30 °C as compared to the first-dimension column oven temperature. The hot-pulse duration was set to 400 ms and the modulation time was 7.5 s.

Helium was used as a carrier gas throughout all experiments.

The flameless burner of the SCD was operated at a temperature of 800 °C and a pressure of 233 Torr (31 kPa absolute pressure). Zero-air and hydrogen were supplied to the burner at 40 and 100 ml/min, respectively. Analog-to-digital conversion of the detector signal was performed at 50 Hz.

3. Results and discussion

3.1. Optimisation of the SCD

Initially, the SCD was set based on the recommendations of the manufacturer. The repeatability and detection limits of the SCD were verified by injecting solutions of dibenzothiophene in xylene. The boiling point of xylene (139 °C) differs enough of that of dibenzothiophene (332 °C) to stay clear of possible solvent effects, which, would have a detrimental effect on the peak shape. In order to be able to directly compare the speed of the SCD to that of the FID, we installed a press-fit effluent splitter (Techrom, Purmerend, The Netherlands) at the end of the analytical column (see Section 2, linear GC experiments). Since the burner of the SCD operates under reduced pressure and the FID at atmospheric pressure, equal splitting between both detectors called for a restriction towards the SCD to be installed. The dimensions of a capillary restriction can be easily calculated using the Poiseuille equation [17]. Performing these calcula-

tions assuming a flow of 0.1 mL/min towards the SCD burner (column flow 0.2 mL/min), a temperature of 200 °C giving a gas viscosity of 2.66×10^{-4} poise, a SCD-burner pressure of 233 Torr (=$3.026e^5$ dynes/cm^2), and a restriction of 2.00 m × 0.10 mm i.d. towards the SCD-burner, this would result in an inlet-pressure for the restriction of 1.12×10^6 dynes/cm^2. This inlet pressure would require a restriction of 39.1 cm with an i.d. of 0.10 mm to also obtain a flow of approximately 0.1 mL/min towards the atmospheric (1 atm = 1.012×10^6 dynes/cm^2) FID. That installing a 200 cm × 0.10 mm i.d. restriction towards the SCD and a 39 cm × 0.10 mm i.d. towards the FID actually results in almost equal splitting between FID and SCD is demonstrated in Fig. 1, where the chromatograms of an injection of a dibenzothiophene solution, under identical chromatographic conditions, before and after the installation of the effluent splitter are presented. At the same time it must be noted that the effluent splitter does not contribute to extra band broadening. Fig. 2 demonstrates the possibility to simultaneously record two detector traces (FID and SCD).

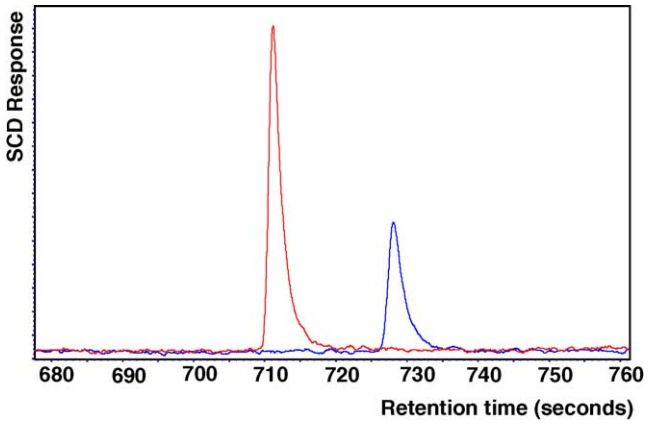

Fig. 1. Chromatogram obtained from a 1 μl split injection of 8.8 mg/kg sulphur (dibenzothiophene in xylene). SCD trace of dibenzothiophene before (red) and after installing a press-fit effluent splitter (blue).

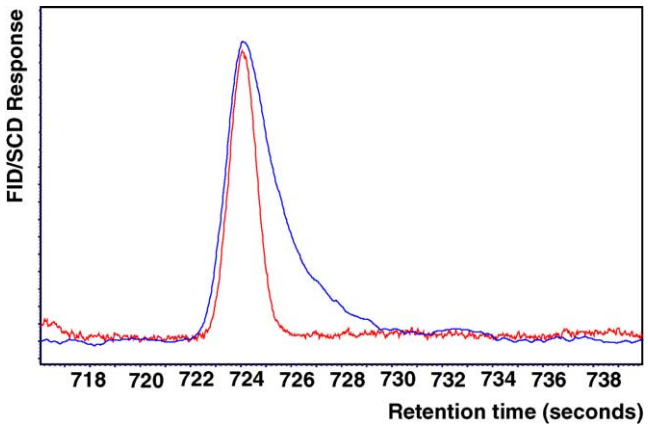

Fig. 2. Chromatogram obtained from a 1 μl split injection of 8.8 mg/kg sulphur (dibenzothiophene in xylene). FID trace (red) and SCD trace (blue) of dibenzothiophene.

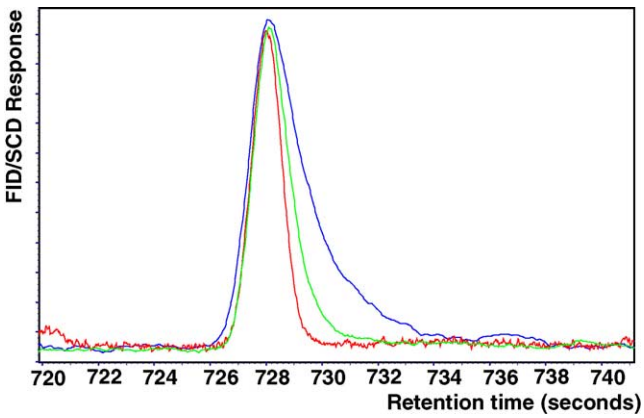

Fig. 3. Chromatogram obtained from a 1 μl split injection of 8.8 mg/kg sulphur (dibenzothiophene in xylene). FID trace (red), SCD trace using the original Sievers amplifier (blue) and SCD trace as recorded with the FPD-500 electrometer (green).

From Fig. 2, it also becomes clearly evident that the FID shows a significantly faster response than the SCD. Clearly, the SCD gives rise to additional band broadening. Strong indications were there, however, that this slow response was caused by system electronics, rather than dead volumes in the chemiluminescence chamber and/or PFA transfer line between burner and reaction chamber [18]. Thanks to the vacuum applied to the reaction chamber, the residence time of the analytes should be approximately 5 ms.

Since the manufacturer Carlo Erba (CE) has the reputation to build relatively fast electrometers/amplifiers [19], it was decided to connect an electrometer intended for use with CE's flame-photometric detector (CE FPD-500 electrometer, Carlo Erba Instruments, Milan, Italy) directly to the photomultiplier tube (PMT) of the SCD system, thus bypassing the entire amplifier electronics of the SCD. The results of this exercise are presented in Fig. 3.

Obviously, the FPD-500 electrometer exhibits faster response characteristics than the original Sievers amplifier, although still not as fast as that of the FID. With the knowledge that the analog amplifier electronics would allow for simple modification to further lower its time constant, it was decided to subject the SCD/FPD-500 combination to a GC × GC experiment. From Fig. 4, in which both the FID and the SCD/FPD-500 trace of a single second dimension separation of a GC × GC kerosene analysis is presented, it becomes evident that the time constant of the FPD-500 electrometer still prohibits proper GC × GC analyses.

After this experiment, the amplification circuitry of the FPD-500 electrometer was modified, following the instructions kindly supplied by its manufacturer (Carlo Erba, Milan, Italy). The effect of these modifications is demonstrated in Fig. 5, where the SCD traces of two single second dimension separations of a kerosene analysis, before, and after having made the modifications, have been overlaid.

In the linear domain, it is difficult to align the SCD and FID signal, firstly because of the delay between SCD-chemiluminescence and FID-ionization detection. Secondly,

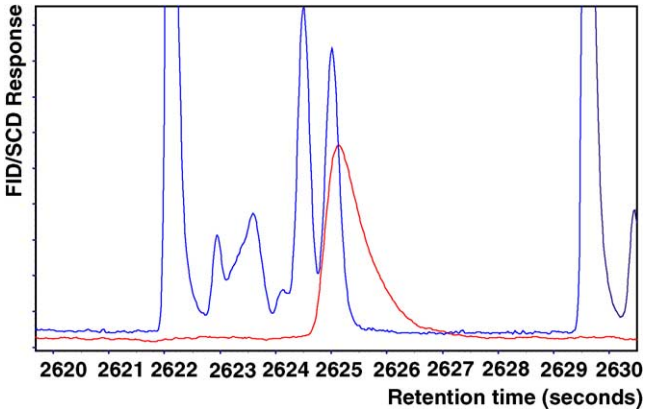

Fig. 4. Chromatogram of a single second-dimension separation of a GC × GC kerosene analysis. FID trace (blue) and SCD/FPD-500 trace (red).

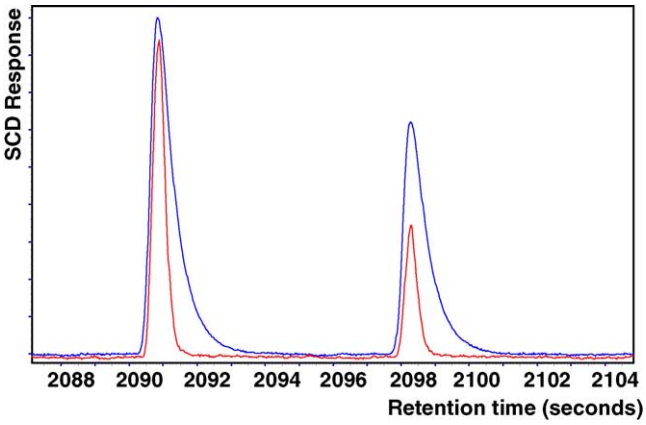

Fig. 5. Chromatogram of two single second-dimension separations of a GC × GC kerosene analysis. SCD/FPD-500 trace before (blue) and after modification (red).

because the FID "sees" the entire matrix, while the SCD only reveals the S-compounds. To compare the speed of the two, however, peaks with similar relative second-dimension retention times, should exhibit similar peak-widths. To demonstrate the speed of the SCD with the modified FPD-500 electrometer as compared to the digital FID in Fig. 6, the SCD- and FID-trace of a GC × GC kerosene analysis have been overlaid.

3.2. Cryogenic modulation

In the experiments discussed thus far, the KT2000 sweeper modulator was used to study and demonstrate the feasibility of GC × GC coupled with fast SCD. This type of modulation, however, has a limited application range in terms of temperature, due to the fact that the refocusing effect in the modulation capillary has to take place at 100 °C above the oven temperature. In the experiments discussed thus far, the maximum allowable temperature of the stationary phase in the modulation capillary limits the application range for high boiling compounds to approximately *n*-C_{28}. Although heated modulation of compounds up to *n*-C_{40} through independent

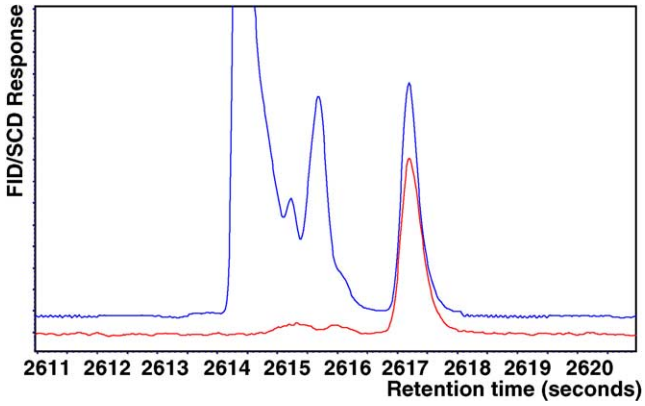

Fig. 6. Single second dimension chromatogram of a GC × GC-FID/SCD kerosene analysis demonstrating the speed of the modified FPD-500 electrometer. FID trace (blue) and SCD/FPD-500 trace (red).

heating of first- and second-dimension column and the use of a "thin"-film modulation capillary has been demonstrated by Frysinger and Gaines [20], this sacrifices the ability to modulate the more volatile compounds (modulation from *n*-C_{10} upwards).

To enable GC × GC–SCD analyses on 'real' samples, the second part of the study employed a ZOEX KT2002 LN_2 loop modulator with pulsed hot jet (ZOEX Corp., Lincoln, NE, USA). Generally speaking, the upper limit of the application range of GC × GC experiments performed with cryogenic modulation is limited solely by the maximum allowable temperatures of the individual columns used. The use of a low-flow cold jet, which utilizes nitrogen gas cooled to near liquid nitrogen temperature, extends the lower limit of the application range down to compounds as volatile as methane [21]. Besides this dramatic extension of the application range, the absence of moving parts in the vicinity of the columns and the use of a single continuously operated cold jet combined with a single pulsed hot jet, makes the loop modulator a simple and robust device. Cryogenic modulation also enables sharper focussing, allowing for even more resolution [21].

3.3. Group-type separation, identification and quantification of sulfur-containing compounds with GC × GC–SCD

The superiority of the GC × GC approach is that, in contrast with most other multidimensional chromatographic techniques, separations can be made truly and fundamentally orthogonal [22]. As with the different classes of hydrocarbons, the main chromatographic difference between the different classes of sulphur-containing compounds is their amenability to polarization. Likewise, sulphur-containing compounds belonging to the same chemical class can therefore also be expected to form bands of spots along the chromatographic plane. In Fig. 7, a GC × GC–SCD chromatogram of a mixture of a light catalytically cracked cycle oil (LCCCO) and a heavy gas oil (HGO) demonstrating such a chemical-class separation is presented. Especially, the bands

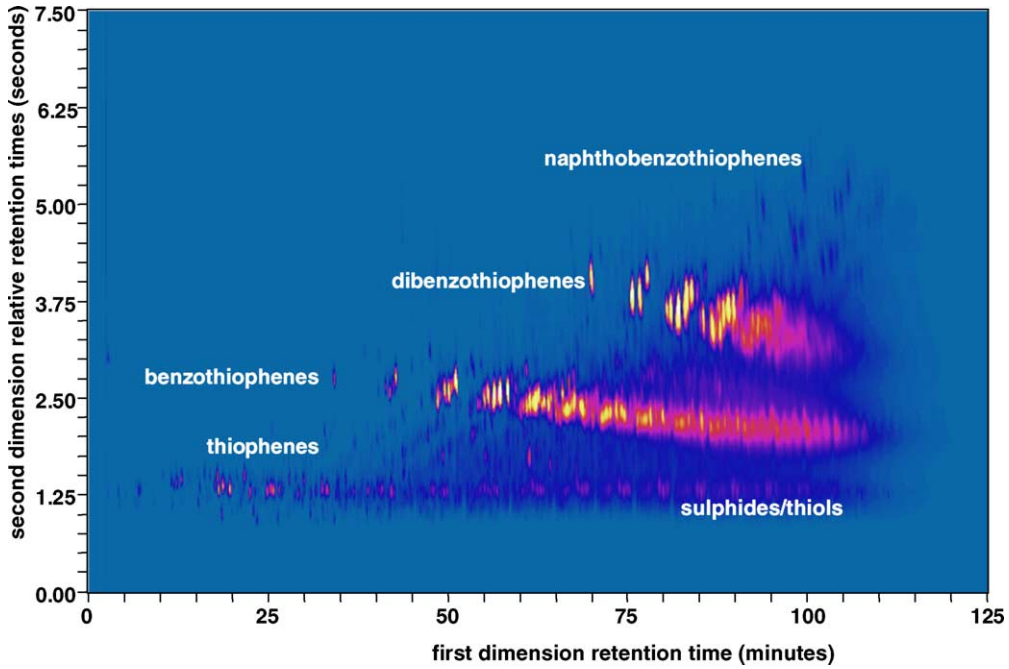

Fig. 7. GC × GC–SCD chromatogram of an LCCCO–HGO mixture.

formed by the aromatic sulphur-species (benzothiophenes, dibenzothiophenes and naphtobenzothiophenes) can readily be discerned. Within these groups, a further speciation according to carbon substitution can be made, aided through the roof-tile effect [23]. Unfortunately the, in some cases highly desirable, separation between the sulphides and thiols is less clear. Although some structure is clearly present, apparently the net effect of the molecular interactions between these species and the stationary phase applied does not allow for a complete group-type separation. Even more structure can be found in the GC × GC–SCD chromatogram of a crude-oil sample from Liverpool Bay, presented in Fig. 8.

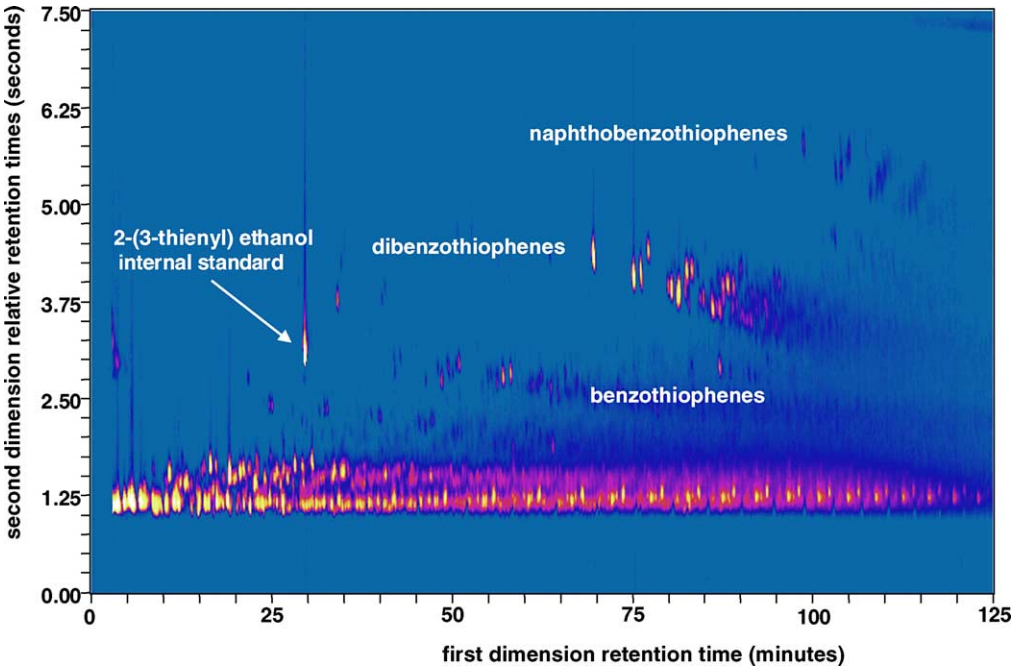

Fig. 8. GC × GC–SCD chromatogram of a Liverpool Bay crude sample.

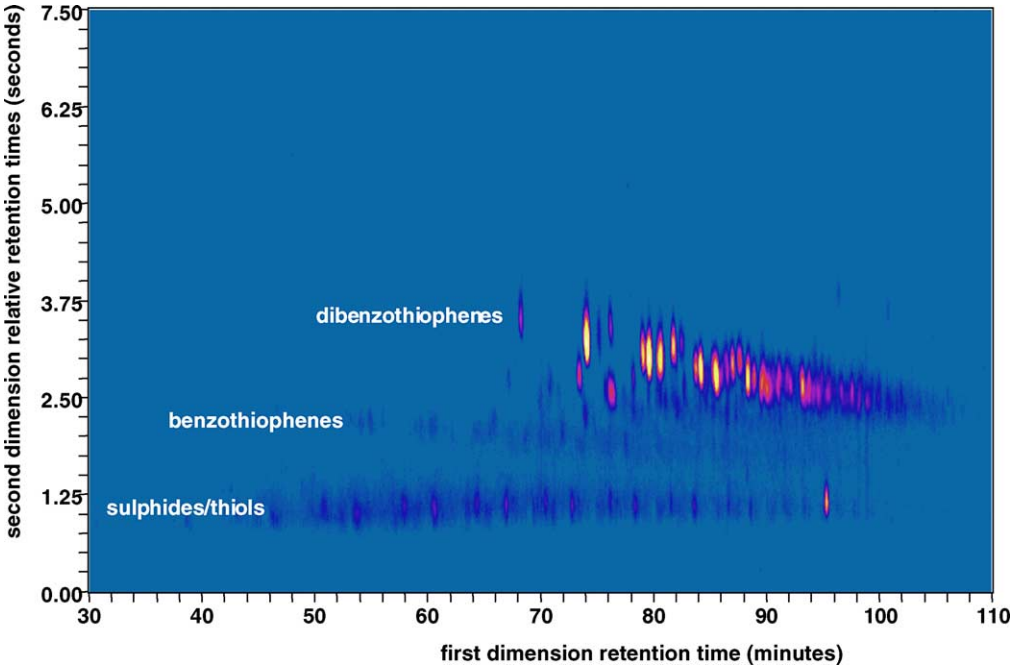

Fig. 9. GC × GC–SCD chromatogram of a desulphurized product stream (25 mg/kg sulphur).

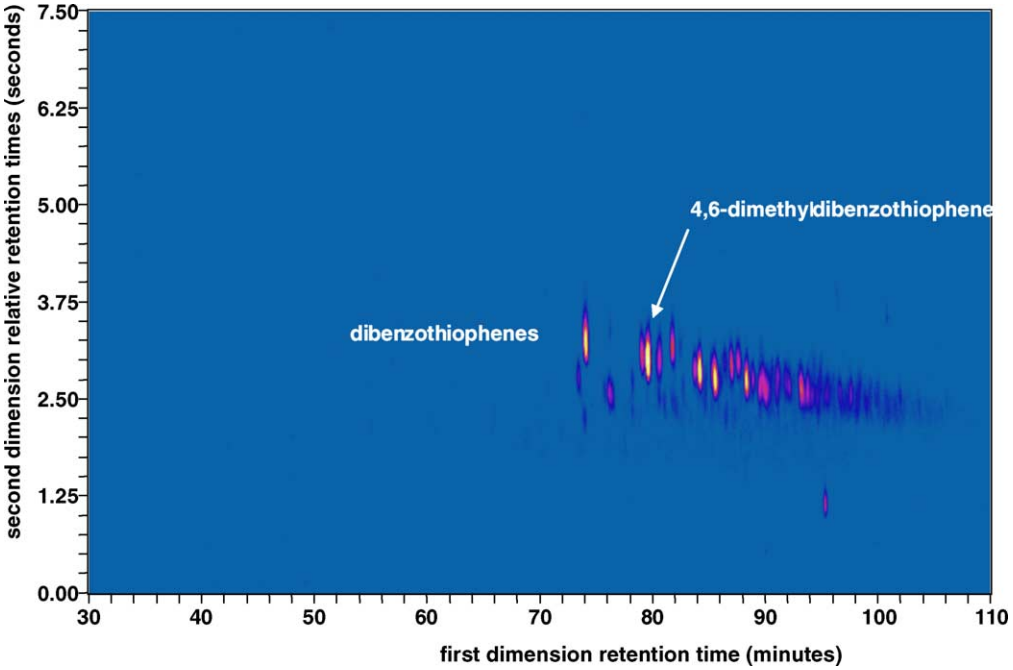

Fig. 10. GC × GC–SCD chromatogram of an HDS product stream (12 mg/kg sulphur) revealing components refractory to HDS.

The enhanced speed of the SCD allows two bands to be readily discerned in the second-dimension relative retention-time region of 1.00–1.75 s. This suggests the separation of two distinct chemical classes. In the upper band, intriguing roof-tile structures can be clearly discerned, even indicating a good match between separator and sample dimensionalities [24]. Attempts to identify these classes through spiking experiments, however, have not (yet) led to firm conclusions.

Fortunately, these classes are of little interest in the study of desulphurization processes as they are the most easily removed. Compounds that are the most refractory to HDS processes are found among the classes of the benzothiophenes and dibenzothiophenes [3,7]. In Fig. 9, a GC × GC–SCD chromatogram of a desulphurized product stream containing 25 mg/kg total sulphur (XRF) is shown. Quantitative analysis by GC × GC–SCD [15] using 2-(3-thienyl)

ethanol as internal standard (^1t_R 18 min, not shown in chromatogram) resulted in 24.3 mg/kg sulphur, which is in good agreement with the total-sulphur content as measured through XRF. Fig. 10 shows the GC × GC–SCD chromatogram of an even deeper desulphurized product stream (total sulphur 12 mg/kg, XRF). In this chromatogram, the position of 4,6-dimethyldibenzothiophene, being one of the compounds known to be most refractory to HDS, was affirmed through spiking experiments. Quantitative analysis yielded 11.4 mg/kg sulphur, which again is in good agreement with the total-sulphur content as obtained through XRF.

Acknowledgments

The authors wish to thank Daniela Cavagnino and Fausto Munari from ThermoFinnigan Italia S.p.A. for their help with the modification of the FPD-500 electrometer.

References

[1] W.L. Orr, C.M. White, Geochemistry of Sulphur in Fossil Fuels, American Chemical Society, Washington, DC, 1990.
[2] S. Cheskis, E. Atar, A. Amirav, Anal. Chem. 65 (1993) 539.
[3] G.C.A. Schuit, B.C. Gates, AlChE J. 19 (1973) 417.
[4] H.C. Lee, J.B. Butt, J. Catal. 49 (1977) 320.
[5] D.R. Kilanowsky, B.C. Gates, J. Catal. 62 (1980) 70.
[6] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. de Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523.
[7] A. Amorelli, Y.D. Amos, C.P. Halsig, J.J. Kosman, R.J. Jonker, M. de Wind, J. Vrieling, Hydrocarbon Process. (1992) 93.
[8] J. Beens, R. Tijssen, J. High Resolut. Chromatogr. 20 (1997) 131.
[9] M. van Deursen, Novel concepts for fast capillary gas chromatography, Ph.D. Dissertation, Technical University Eindhoven, Universiteitsdrukkerij Eindhoven, The Netherlands, 2002.
[10] J. Dallüge, J. Beens, U.A.Th. Brinkman, J. Chromatogr. A 1000 (2003) 69.
[11] L.L.P. van Stee, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 1019 (2003) 89.
[12] F.C. Wang, W.K. Robbins, F.P. Di Sanzo, F.C. McElroy, J. Chromatogr. Sci. 41 (2003) 519.
[13] R. Hua, Y. Li, W. Liu, J. Zheng, H. Wei, J. Wang, X. Lu, H. Kong, G. Xu, J. Chromatogr. A 1019 (2003) 101.
[14] J.B. Phillips, R.B. Gaines, J. Blomberg, F.W.M. van der Wielen, J.-M. Dimandja, V. Green, J. Granger, D. Patterson, L. Racovalis, H.-J. de Geus, J. de Boer, P. Haglund, J. Lipsky, V. Sheena, E.B. Ledford Jr., J. High Resolut. Chromatogr. 22 (1999) 3.
[15] V.G. van Mispelaar, A.C. Tas, A.K. Smilde, P.J. Schoenmakers, A.C. van Asten, J. Chromatogr. A 1019 (2003) 15.
[16] Diane Nicholas, Procedure of Using the OPTIC 2 for Selective Exclusion, ATAS Chromatography Technical Note 18 A, ATAS, Cambridge, UK.
[17] W.J. Moore, Physical Chemistry, fourth ed., Prentice-Hall, 1972.
[18] R. Shearer (Sievers Instruments, Boulder, CO, USA), Personal communication, Januari 2001.
[19] C.P.M. Schutjes, High speed, high resolution capillary gas chromatography: Columns with a reduced inner diameter, Ph.D. Thesis, Technical University Eindhoven, 1983, p. 47.
[20] G.S. Frysinger, R.B. Gaines, J. Sep. Sci. 24 (2001) 87.
[21] E.B. Ledford Jr., Patent WO 2003082427 A1 (2003).
[22] J. Blomberg, J. Beens, P.J. Schoenmakers, R. Tijssen, J. High Resolut. Chromatogr. 20 (1997) 539.
[23] J. Beens, J. Blomberg, P.J. Schoenmakers, J. High Resolut. Chromatogr. 22 (1999) 19.
[24] J.C. Giddings, J. Chromatogr. A 703 (1995) 3.