Investigation of sulphur compounds in coal tar using monodimensional and comprehensive two-dimensional gas chromatography

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ABSTRACT

Coal is a non renewable fossil fuel, used mainly as a source of electrical energy and in the production of coke. It is subjected to thermal treatment, pyrolysis, which produces coke as a main product, in addition to a condensed liquid by-product, called tar. Tar is a complex mixture of organic compounds which contains different chemical classes, presenting aromatic and sulphur heterocyclic compounds. In general, identification of these compounds requires steps of isolation and fractionation, mainly due to co-elution of these compounds with polyaromatic hydrocarbons (PAH). The objective of this work is to characterize the sulphur compounds present in the coal tar obtained via pyrolysis, using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry detector (GC × GC/TOFMS). Coal samples from the State of Paraná, Brazil were subjected to laboratorial scale pyrolysis. Several experimental conditions were tested, such as sample weight (5, 10 and 15 g), heating ramp (10, 25 and 100 °C/min) and final temperature (500, 700 and 900 °C). Samples were analyzed by one dimensional gas chromatography (1D-GC) coupled to a quadrupole mass spectrometry detector (GC/qMS) and two-dimensional gas chromatography with time-of-flight mass spectrometry detector (GC × GC/TOFMS). The higher amount of sulphur compounds was obtained at a final temperature of 700 °C and a heating ramp of 100 °C/min. The main classes observed in the color plot were thiophenes, benzothiophenes and alkylated dibenzothiophenes. GC × GC/TOFMS allowed the identification of the greater number of compounds and the separation of several sulphur compounds from one another. Moreover, separation of sulphur compounds from polyaromatic hydrocarbons and phenols was achieved, which was not possible by 1D-GC. Comparing GC × GC/TOFMS and 1D-GC (SIM mode) also showed that 1D-GC, one of the most employed quantification tools for sulphur compounds, can be misleading for detection, identification and quantification, as the number of isomers of sulphur compounds found was greater than theoretically possible.

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1. Introduction

Despite its relatively low content, sulphur is one of the most important elements of coal that characterizes its quality. It is found in coal either in the form of inorganic compounds, chiefly as pyrite and sulphides or present as organic sulphur. The content of organic sulphur compounds (OSC) in coal is partially conditioned to its presence in the original vegetable material from which coal deposits were formed. This part of sulphur in coal is known as the original organic sulphur.

Currently, coal is still one of the major resources in the world for energy generation [1,2]. The emission of pollutants during its combustion is the main concern, which prevents an even larger utilization. The process of burning coal releases SO_x to the atmosphere (90% as SO_2 and 10% as SO_3) [3], causing deleterious effects

such as formation of acid rain and corrosion of metallic equipment [2]. It can also be harmful to human health, including respiratory diseases such as asthma, bronchitis, emphysema and pneumoconiosis. These problems caused by the presence of sulphur in coal indicate the need of an effective desulphurization process. While physical and chemical methods are available for the removal of a great deal of the inorganic sulphur species, the organic sulphur has proved to be more difficult to remove [4]. Much research and technological development efforts have been devoted to this objective [4,5], but no entirely technical or economical satisfactory solution has been found so far [4].

In general, coal is subjected to thermal treatment, pyrolysis, which produces coke as a main product, in addition to a condensed liquid by-product, called coal tar [6]. Coal tar is a very complex mixture of organic compounds, consisting of components with different functionalities, presenting polycyclic aromatic hydrocarbons (PAH) as dominant compounds [7]. In addition to PAH, homologous heterocyclic compounds containing oxygen, nitrogen and sulphur are also present in small amount [7]. Organic sulphur also occurs in

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the form of aliphatic or aromatic thiols, sulphides, disulphides, and heterocyclic combinations as thiophenes or dibenzothiophenes [8]. Due to low concentrations of OSC and to their co-elution with PAH [9], their identification usually requires steps of isolation and fractionation [10].

Most studies on sulphur compounds in coal, refer to the process variables involved in pyrolysis [11–14]. Detailed work on characterization and identification of organic sulphur using gas chromatography are not common in the scientific literature [15–17].

The lack of knowledge in relation to organic molecular structures of sulphur compounds in coal and/or coal tar results in greater difficulties when searching for a cost-effective process for complete removal of OSC. Thus, the characterization and identification of these compounds in coal are of great importance [4]. The development and application of new approaches for preparation, fractionation and chromatographic analysis of fractions derived from coal and/or coal tar are important and present difficult analytical challenges, since these components are located in complex matrices and are present in great variety and low concentration. All these characteristics increase the likelihood of co-elutions between analyte/analyte and among analytes/interfering matrix components. Furthermore, the environmental and toxicological importance of these compounds place greater emphasis on the analytical method development. 1D-GC with selective detectors is largely employed for organic sulphur compound analysis. Selective detectors, such as sulphur chemiluminescence detector (SCD), pulsed flame photometric detector (PFPD) and atomic emission detector (AED) are the detectors of choice for the analysis of sulphur compounds in fossil fuels [18]. Their limits of detection (LOD) are in the range of 0.5 pg S/s [19]. Quadrupole mass spectrometry detector (qMS) is also employed as it provides structural information. On the other side, a time-of-flight mass spectrometer (TOFMS) gives structural information, providing clean spectra also of partially co-eluting compounds, through mass spectral deconvolution. It is ideal for very narrow peaks (typically 100–200 ms width at the base), as its acquisition rate may reach 500 spectra/s [20]. Given the limitations of one dimensional gas chromatography (1D-GC), the use of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry detector (GC × GC/TOFMS) can bring analytical advances in regards to the elucidation of a larger number of OSC in these matrices. GC × GC may result in increased peak capacity, greater sensitivity, and resolution, higher mass spectral quality, and ordered distribution of OSC peaks in the chromatographic space, ensuring more analytical information. In addition to the increased chromatographic resolution inherent to the GC × GC technique, the deconvolution software of the TOFMS instrument still increases the system capability for the resolution of overlapping peaks [21]. GC × GC has previously been applied to a number of fossil fuel samples, especially petroleum [21–26], but very little has been reported for the characterization of coal [23].

This work is the first attempt to identify a larger number of OSC in pyrolysed coal through the use of GC × GC/TOFMS.

2. Experimental

2.1. Coal samples

The coal sample was collected from a coal field in Cambuí, Figueira city, State of Paraná, Brazil. The sample was reduced to powder and passed through a 200 mesh sieve (75 μm), being dried at 105 °C, according to NBR 8293. Determination of the forms of sulphur (pyritic, sulphatic, organic and total sulphur) and proximate analysis were performed for all samples, according to standard methods [27,28]. Carbon, hydrogen, and nitrogen contents were

Table 1
Global composition and elemental analysis of coal.

| Proximate analysis	Average content (%)	Ultimate analyses	Average content (%)
Ash	29.8	Carbon	42.4
Volatile matter	28.3	Hydrogen	2.9
Fixed carbon	41.9	Nitrogen	0.9
		Total sulphur	2.8
		Pyritic sulphur	1.7
		Sulphatic sulphur	0.2
		Organic sulphur	0.9

determined using a Leco CHN-600. Physicochemical characteristics of coal are summarized in Table 1.

2.2. Pyrolysis apparatus and procedure

Pyrolysis experiments were carried out under nitrogen atmosphere in a tubular oven with a reactor made of quartz, with a diameter of 40 mm and 1200 mm in length. A temperature controller type N-480 Novus with K-type relay and 1.7 kW of power was employed to control oven temperature and the internal parts of the quartz reactor as in Fig. 1. Three different amounts of coal were employed during pyrolysis (10, 15 and 20 g). The coal amount that rendered higher yield of tar was chosen to be used in all pyrolysis runs. The reactor was placed inside the oven and heated up to the desired final temperature (500, 700 or 900 °C), using temperature ramps such as 10, 20 or 100 °C/min. Pyrolysis was immediately stopped after reaching the final temperature or temperature was kept constant for 10 min. The tar was cooled and solutions of 10 g l^{-1} were prepared in dichloromethane. These solutions were diluted to 1 g l^{-1} and analyzed in a gas chromatograph with a mass spectrometry detector.

2.3. Analysis of coal tar using gas chromatography coupled to a quadrupole mass spectrometry detector (GC/qMS)

Analysis of coal tar solutions were carried out with a Shimadzu Gas Chromatograph gas chromatograph instead of Gas Chromatograph coupled to a quadrupole mass spectrometry detector QP-5050A (GC/qMS). It was equipped with a DB5-MS column (5% phenyl–95% dimethylpolysiloxane, J&W-Agilent, Folsom, CA, USA) of 30 m length, 250 μm I.D., and 0.25 μm of phase thickness. The initial oven temperature was maintained at 40 °C for 1 min and then increased to 280 °C at 4 °C/min and kept at this final temper-
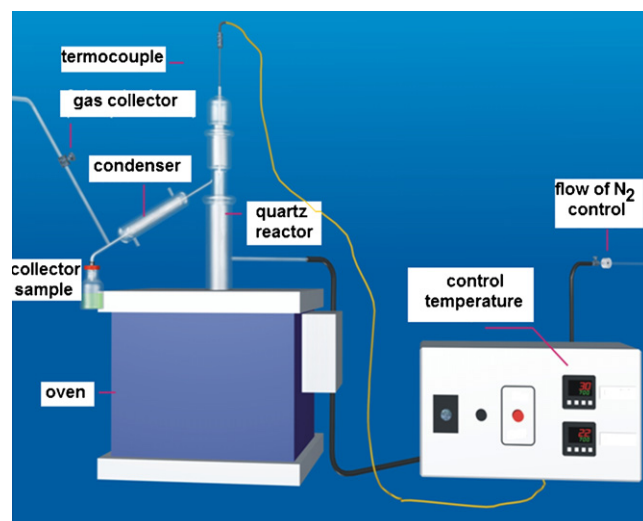
Fig. 1. Scheme of the pyrolysis set-up.

ature for 5 min. The carrier gas was helium (Linde Gases, Canoas, Brazil, 99.999% purity) supplied at of 1.8 ml min^{-1} and a 1 μL of each sample was injected, keeping the injector at 280 °C in split-less mode. Quadrupole mass spectrometry detector was operated in scan mode (45–500 u), using 70 eV during electronic impact and keeping its interface at 280 °C. Whenever convenient, the detector was also employed in a single ion monitoring mode (SIM).

2.4. Analysis of coal tar using two-dimensional gas chromatograph with time-of-flight mass spectrometry detector (GC × GC/TOFMS)

A GC × GC/TOFMS Pegasus-IV system (LECO, St. Joseph, USA) equipped with a liquid nitrogen quad-jet modulator and CTC Combi Pal autosampler was used. The following columns were employed in the first and second dimension, respectively: a DB5 column (5% phenyl–95% dimethylpolysiloxane) of 30 m length, 250 μm I.D. and 0.25 μm of phase thickness and a DB-17ms column (50% phenyl–50% dimethylpolysiloxane) of 1.9 m length, 0.18 mm I.D, and 0.18 μm of phase thickness (Agilent Technologies, J&W Scientific, Agilent, Folsom, CA, USA). The carrier gas was helium under a constant flow rate of 1 ml min^{-1} and the volume of sample injected was 1 μL. The injector temperature was 280 °C and samples were injected in splitless mode. The temperature program of the first column started at 40 °C for 1 min and reached a final temperature of 280 °C at 4 °C/min, where it was kept for 5 min. Transfer line was held at 280 °C and the electron impact ionization source itself was operated at 250 °C with collision energy of −70 eV. Detector voltage was −1587 V, mass range was 45–500 amu and data acquisition rate was 100 Hz. Several modulation periods (3, 5, 6, 8, 10 and 12 s) and oven's offset temperatures (5, 10, 15 °C) were tested. Hot pulse was 45% of modulation period and data processing was achieved using integrated Leco ChromaTOF software, version 3.32.

2.5. Procedure adopted for comparative study GC/qMS and GC × GC/TOF-MS

The study of sulphur compounds in the chromatograms was initially performed using characteristic ions of these compounds in the extracted ion mode (EIM), both in 1D-GC and GC × GC. In the following step, confirmation of their presence was made by comparing their full mass spectra with those of the 6th edition of Wiley (for 1D-GC) and of NIST (for GC × GC) libraries. A similarity matching above 70% between the unknown spectrum and the library spectrum was requested in order to confirm the identity of sulphur compounds.

3. Results and discussion

3.1. Pyrolysis yield

Yield (m/m) obtained for each pyrolysis procedure is presented in Table 2. The use of 15 g of coal resulted in better yield than 10 and 20 g (experiments 1, 2, and 3 in Table 2), and was chosen for all other experiments carried out. The best yield was achieved when the highest final temperature and heating rate were employed. According to Baruah and Khare, higher yields of sub-bituminous coal tar were also obtained at higher final temperatures, between 850 and 1000 °C [12].

3.2. Analysis of coal tars by GC/qMS and GC × GC/TOFMS

Literature reports that the amount of sulphur in coal derived liquids is low and depends on the type, origin, and geographic locality of the coal source [29–31]. Co-elutions with polyaromatic hydrocarbons (PAH) are common in this type of matrix, and PAH are usually present in higher amounts than sulphur compounds,

Table 2
Yields of coal tar for different experimental pyrolysis conditions.

Experiment	Mass (g)	ΔT–°C (t_{final}, min)	Rate (°C/min)	Yield (%)
1	10	T_{amb}–700 (*)	20	1.2
2	15	T_{amb}–700 (*)	20	4.5
3	20	T_{amb}–700 (*)	20	3.8
4	15	T_{amb}–900 (10)	10	1.8
5	15	T_{amb}–900 (10)	10	2.3
6	15	T_{amb}–700 (*)	10	3.5
7	15	T_{amb}–700 (10)	10	3.7
8	15	T_{amb}–500 (*)	10	3.1
9	15	T_{amb}–500 (10)	10	3.2
10	15	T_{amb}–900 (*)	100	4.5
11	15	T_{amb}–900 (10)	100	4.5
12	15	T_{amb}–700 (*)	100	2.3
13	15	T_{amb}–700 (10)	100	2.9
14	15	T_{amb}–500 (*)	100	4.2
15	15	T_{amb}–500 (10)	100	4.3

T_{amb}: ambient temperature; t_{final}: final temperature was kept for this time interval; (*) pyrolysis process was immediately stopped after reaching final temperature.

rendering an even more challenging detection and identification process [32]. This information complies with results in this work, since the number of sulphur compounds found in the fifteen coal tar samples (Table 2) analyzed by GC/qMS in scan mode was low or nonexistent. The same samples were also analyzed by GC × GC/TOFMS and better results were achieved as shown in Table 3. The total number of constituents detected was 109 and 564 for 1D-GC and GC × GC, respectively, considering a minimum signal to noise ratio (S/N) of three for both techniques. Experiment 12 rendered the highest number of sulphur compounds and was chosen for a more detailed 1D-GC study using SIM mode. 1D-GC and GC × GC chromatograms are shown in Fig. 2. Among all tests made for different modulation periods and secondary oven's off-set, a superior structural effect was achieved in the 2D separation space when 12 s and 10 °C were employed. Wrap around effect was observed in each one of the tested conditions.

Results obtained by 1D-GC showed co-elutions among various sulphur compounds and also among these analytes and compo-
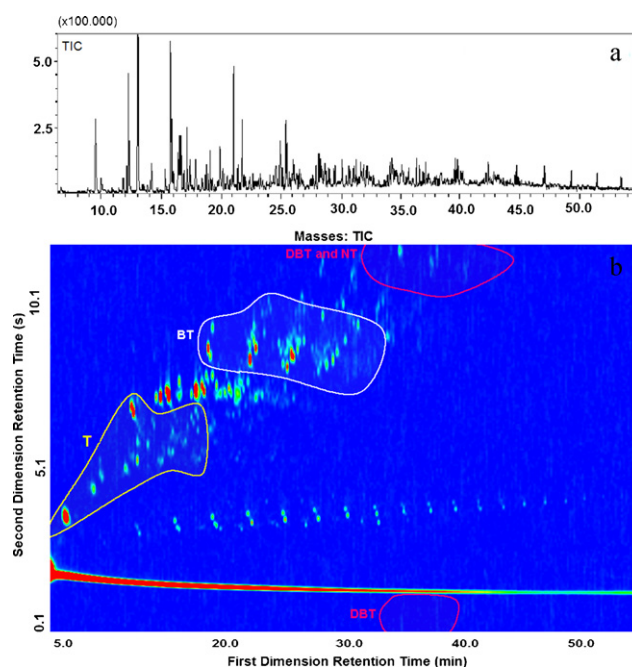
Fig. 2. 1D-GC/qMS total ion current chromatogram (a) and GC × GC/TOFMS color plot (b). Chromatographic conditions are described in Section 2. Regions are assigned for thiophenes (T), benzothiophenes (BT), dibenzothiophenes and naphthothio-phenes (DBT and NT). Wrap around is observed for the region of elution of DBT.

Table 3
Sulphur compounds tentatively identified in coal tars obtained with different pyrolysis conditions using GC × GC/TOFMS.

Experiment	Sulphur compounds (number of isomers)	T[a]
1	C1-benzothiophene (2), C3-benzothiophenes	3
2	C3-thiophene, benzothiophene, C1-benzothiophene, C2-benzothiophenes (3), C3-benzothiophenes (3)	9
3	cyclopentathiapyran, C1-benzothiophenes (4), C2-benzothiophenes (2), C3-benzothiophenes (2)	9
4	cyclopentathiapyran, C1-benzothiophenes (3), C2-benzothiophene	5
5	benzothiophene, C1-benzothiophenes (2)	3
6	cyclopentathiapyran, C1-benzothiophene, C2-benzothiophenes (3)	5
7	C3-thiophene, benzothiophene, C1-benzothiophene	3
8	C3-thiophenes (3), benzothiophene, C1-benzothiophenes (3), C2-benzothiophenes (3), C3-benzothiophenes (2)	12
9	C3-benzothiophenes (2), benzothiophene, C1-benzothiophene, C2-benzothiophenes (2)	6
10	C2-thiophenes (2), C3-thiophene, cyclopentathiapyran, C1-benzothiophenes (2), C2-benzothiophene, C3-benzothiophenes (2), dibenzothiophene	10
11	C2-thiophene, C3-thiophene, cyclopentathiapyran, benzothiophene, C1-benzothiophene, C2-benzothiophenes (2), C3-benzothiophenes (3), dibenzothiophene, thioxanthene	12
12	C2-thiophenes (2), C3-thiophenes (3), cyclopentathiapyran, C1-benzothiophene, C2-benzothiophenes (3) C3-benzothiophenes (4), C4-benzothiophene, dibenzothiophene, C1-dibenzothiophene, thioxanthene	18
13	No compound was detected due to technical problems	
14	C3-thiophene, cyclopentathiapyran, benzothiophene, C1-benzothiophenes (3), C2-benzothiophenes (4), C3-benzothiophenes (2)	12
15	C2-thiophene, C3-thiophene, benzothiophene, C1-benzothiophenes (2), C2-benzothiophenes (4) C3-benzothiophenes (2)	11

[a] T: Total number of sulphur compounds tentatively identified.

nents of other classes, such as aromatics, phenols, and polyaromatic hydrocarbons.

Comparison among mass spectra of coal tar sulphur components and mass spectra of commercial libraries showed higher similarity and consequently higher spectral purity when using GC × GC/TOFMS than with 1D-GC/qMS (Table 4). Similar results were observed with the application of GC × GC/TOFMS to other complex matrices [32–34].

Results of previous research efforts for the characterization of sulphur compounds in different matrices, such as oil and derivatives, were used for the sake of comparison. Some researchers have applied different stationary phases (containing cyanopropyl, biphenyl and liquid crystalline) to separate some components that co-elute when the most used stationary phase (5% phenyl–95% dimethylpolysiloxane) is employed. In these cases, two chromatographic analyses were required, using the same sample, one in each stationary phase, increasing analysis time and making the separation process more laborious [10,34]. Sulphur compounds of coal tar obtained in experiment number 12 (Table 2) are described below, according to their chemical classes: thiophenes, dibenzothiophenes, and benzothiophenes.

3.2.1. Thiophenes

Selecting m/z 126 as the characteristic ion of thiophenes with three methyl groups (C3-T), it was possible to tentatively identify five C3-T using GC × GC. A structurally dependent ordered distribution of chromatographic peaks is observed in Fig. 3c. Two out of the three trimethyl-thiophenes (TriMe-T) isomers are located more to the right of the color plot (yellow line circle), while three of the other are methyl ethyl thiophenes isomers (MeEt-T) and are located more to the left of the color plot (white line circle). The MeEt-T may be: 2-Me-3-Et-T, 2-Et-3-Me-T, 4-Et-2-Me-T, 2-Et-5-Me-T, 2-Et-4-Me-T, 2-(1-MeEt)-T, and 3-(1-MeEt)-T. Distinction between these two clusters of compounds was based on their characteristic mass spectra. Fig. 3c shows the GC × GC color plot resulting from the full mass spectra of coal tar, where a dominant phenol peak is seen around the same t_{R1} of a less intense sulphide compound peak. Fig. 3a shows that the phenol peak superposes a minor peak of a sulphide compound, decreasing the quality of its mass spectrum (70% of mass spectra similarity to 1D-GC/qMS and from 86% to 74% to GC × GC/TOFMS, according to Table 4). Co-elution of phenol and sulphide compounds has not been reported in the scientific literature to date. Also co-elution of sulphide compounds and trimethyl ben-

zene was observed. In both cases, no sulphur compounds presented higher intensity.

3.2.2. Benzothiophenes

Fig. 4 shows the region where methyl benzothiophenes (C1-BT) elute. The 1D-GC chromatogram shows a major peak for methylnaphthalene (C1-N, t_{R1} and t_{R2} = 23.35 min and 8.49 s) and a front shoulder that corresponds to a methyl benzothiophene (C1-BT, t_{R1} and t_{R2} = 23.35 min and 8.93 s). GC × GC showed (Fig. 4b) better chromatographic separation of these two compounds. A similar situation is observed for another C1-BT isomer eluting on t_{R1} of 23.95 min. In this case, the signal intensity of the aromatic compound is also higher than the one of C1-BT, making it difficult to detect or identify by 1D-GC. Co-elutions of polycyclic aromatic sulphur heterocycles (PASH) and PAH were already described in the scientific literature and are an analytical challenge, which has been partially solved by using more than one stationary phase in 1D-GC, rendering a more laborious, tedious, and time consuming chromatographic procedure [32]. The selection of the characteristic ion of C1-BT, m/z 148, enabled the visualization of five out of six possible chromatographic peaks shown in Fig. 4c. The peak shape of one of them gives an indication of a possible co-elution. Andersson and Schmid [10] reported that separation of these isomers and others (3-, 4-, 5-, and 6-methyl benzothiophenes) in 1D-GC, using dimethylpolysiloxane stationary phase with 5% phenyl or 30% biphenyl was difficult.

The greatest challenge was the separation of four C1-BT. 3- and 4-methyl benzothiophene and the pair 5- and 6-methyl benzothiophene. A better result was achieved with a cyanopropyl column, however, the upper temperature limit of this stationary phase is 250 °C, which hinders the analysis of higher molecular weight OSC, as for example, sulphur containing four aromatic rings (benzonaphthothiophenes—BNT). Mössner and Wise [33] used a liquid crystalline stationary phase to separate the BNT, a 50% phenyl–50% dimethylpolysiloxane to separate naphtothiophenes and a 5% phenyl–95% dimethylpolysiloxane to separate other compounds, which is obviously a laborious and time consuming procedure.

A similar case (figure not shown) was found for the benzothiophenes with two methyl (C2-BT), which co-elute with dimethyl naphthalenes (C2-N). Anderson and Schmid [10] also reported co-elution problems for these PASH and PAH. The selection of m/z 162 as a characteristic ion enabled the identification of seven sul-

Table 4
Sulphur compounds tentatively identified using 1D-GC/qMS and GC × GC/TOFMS for sample number 12 (Table 3).

Ions[a]	1D-GC/qMS			GC × GC/TOFMS		
	Compound name	t_R	Similarity[b]	t_R		Sim
				^{1}D	^{2}D	
111, 126	C3-Thiophene	9.6	70	11.3	5.4	74
	C3-Thiophene			11.7	5.7	80
	C3-Thiophene			12.1	5.5	85
	C3-Thiophene			12.7	6.0	70
	C3-Thiophene			13.1	6.2	86
134	Benzothiophene	17.4	89	19.7	9.5	91
147, 148	C1-Benzothiophene	20.8	70	22.9	9.3	89
	C1-Benzothiophene	21.6	79	23.1	9.0	90
	C1-Benzothiophene			23.3	8.9	90
	C1-Benzothiophene			23.5	9.2	70
	C1-Benzothiophene			23.7	9.5	90
162, 161	C2-Benzothiophene	24.4	77	26.3	8.7	86
	C2-Benzothiophene			26.5	8.9	75
	C2-Benzothiophene	25.2	79	26.9	8.7	86
	C2-Benzothiophene			26.9	9.0	84
	C2-Benzothiophene	24.9	78	27.3	9.1	83
147, 162	C2-Benzothiophene			27.5	9.3	82
	C2-Benzothiophene			27.7	9.0	76
161, 176	C3-Benzothiophene			29.1	8.6	80
	C3-Benzothiophene			29.7	8.4	84
	C3-Benzothiophene		72	29.9	8.7	87
	C3-Benzothiophene	28.6	78	30.1	8.4	71
176, 161	C3-Benzothiophene	29.2	73	30.3	8.6	72
	C3-Benzothiophene			30.5	8.7	78
	C3-Benzothiophene			30.9	8.9	77
	C3-Benzothiophene			31.1	8.7	78
	C3-Benzothiophene			31.3	9.1	82
	C3-Benzothiophene			31.5	9.1	74
175, 190, 147	C4-Benzothiophene			32.7	8.4	72
175, 190, 141	C4-Benzothiophene			32.5	8.3	76
175, 190, 160	C4-Benzothiophene			33.1	8.7	72
175, 190, 141	C4-Benzothiophene			33.3	8.4	74
	C4-Benzothiophene			33.5	8.5	71
	C4-Benzothiophene			34.1	8.7	73
	C4-Benzothiophene			35.1	8.9	72
184, 139, 152	Dibenzothiophene	35.6	76	37.9	0.5	90
184, 139, 152	Naphthobenzothiophene			38.5	0.9	89
	Naphthobenzothiophene			36.9	11.8	89
	Naphthobenzothiophene			37.1	0.2	89
198, 197	C1-dibenzothiophene	38.9	77	39.5	11.4	83
	C1-dibenzothiophene			40.1	11.2	82
	C1-dibenzothiophene			40.5	11.7	78
	C1-dibenzothiophene			40.7	11.6	91
197, 198	Thioxanthene			41.3	0.1	78
212, 211, 197, 178	C2-dibenzothiophene			42.1	10.9	77
212, 211, 197, 165	C2-naphtho [2,3-b] thiophene			42.5	10.8	70
212, 211, 197, 105, 152	C2-dibenzothiophene			42.7	10.9	82
	C2-dibenzothiophene			43.1	11.2	81
	C2-naphtho [2,3-b] thiophene			43.3	11.2	81
	C2-dibenzothiophene			43.9	11.7	77

[a] Characteristic ions in order of importance.
[b] Similarity between the mass spectrum of the coal tar compound and the one in commercial mass spectra libraries.
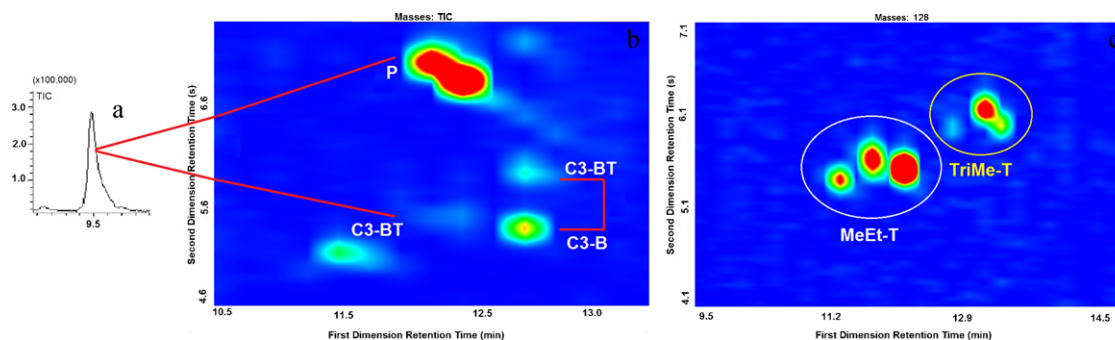
Fig. 3. 1D-GC total ion current chromatogram (a); GC × GC color plot (b) for the region of thiophenes with three methyl groups (C3-T), indicating co-elutions of C3-T with P (phenol) and with C3-B (trimethyl benzene); (c) GC × GC color plot of the characteristic ion *m/z* 126. MeEt-T (methyl ethyl thiophene); TriMe-T (trimethyl thiophene).
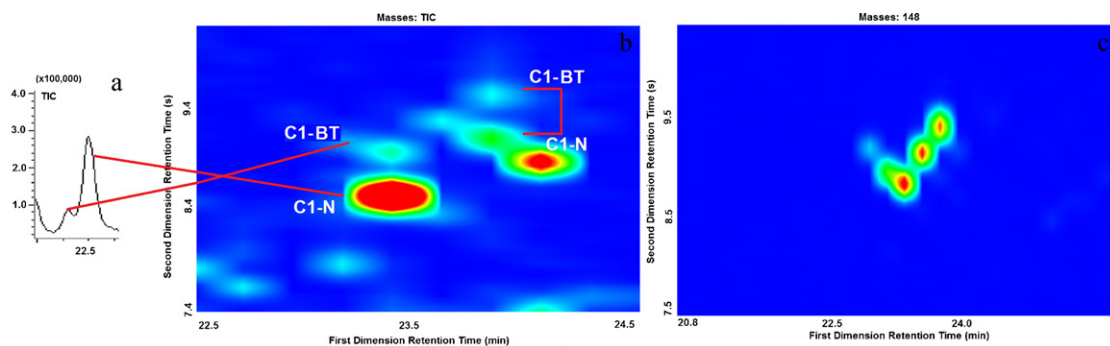
Fig. 4. Total ion current chromatograms for 1D-GC (a) and GC × GC diagram (b) for the region of methyl-benzotiophenes (C1-BT), indicating co-elutions with methyl naphthalene (C1-N). (c) GC × GC color plot of the characteristic ion *m/z* 148.

phur compounds out of 15 possible for this class of compounds, suggesting a higher sensitivity and peak capacity of GC × GC.

Fig. 5 shows the region where benzothiophenes with three methyl groups (C3-BT) elute. These compounds were not detected by 1D-GC in the scan mode (Fig. 5a$_1$). However, a peak corresponding to C3-BT (Table 4) was detected when extracted ion mode was employed (Fig. 5a$_2$). Analysis by GC × GC showed the separation of a trimethyl-naphthalene (C3-N) isomer from a trimethyl-benzothiophene (TriMe-BT). The sulphide compound was the most retained in 50% phenyl phase. Once again, the signal intensity of the aromatic compound is well above the OSC, which complicates its detection by 1D-GC.

The selection of the ion characteristic of C3-BT (*m/z* 176) allowed the visualization of 10 chromatographic peaks, as shown in Fig. 5c, and only one was detected by 1D-GC. It is known that there are 20 isomers for TriMe-BT (most intense ion *m/z* 176, followed by *m/z* 161), 30 isomers for ethyl methyl benzothiophene (EtMe-BT) (most intense ion *m/z* 161, followed by *m/z* 176), six isomers for propyl benzothiophene (Prop-BT) (most intense ion *m/z* 147, followed by *m/z* 176) and 6 for isopropyl benzothiophenes (Isoprop-BT). TriMe-BT and EtMe-BT were tentatively identified and distinguished among them through differences in their mass spectra. According to Depauw and Froment [34] some of the TriMe-BT, EtMe-BT, and Prop-BT of light oil co-elute in a 100% polydimethylsiloxane column. A major presence of TriMe-BT and EtMe-BT in the pyrolysed coal sample was found and Prop-BT was not detected.

No compound was found, when GC/qMS was used in the selective ion mode (SIM) for the characteristic 190 ion of benzothiophenes with four carbons (C4-BT). Analyzing the same sample by GC × GC/TOFMS, a co-elution of dibenzopyrane and one more intense peak of C4-benzene (C4-B) in ^{1}D was observed (figure not shown). Difference in intensity among the peaks turns the visualization of dibenzopyrane in the color plot into a difficult task. Seven C4-BT appeared when the characteristic ion (*m/z* 190) was chosen (figure not shown). The advantage of GC × GC/TOFMS over 1D-GC is specially seen in this case, as C4-BT, TriMe-N and C4-B present a 190 ion in common. In case of their co-elution in 1D-GC, the sum of all these compounds would contribute to the peak area of the sulphur compound, resulting in an overestimation of its content. It is important to mention that the ion 190 is less intense in the mass spectrum of PAH than in PASH, however the presence of this common ion might cause problems in a quantitative analysis, as the chromatographic signal of PAH is the most intense in several samples. In GC × GC, however, it is possible to separate these compounds, preventing the sum of the ions of TriMe-N and C4-B from the ones of the C4-BT.

3.2.3. Dibenzothiophenes

Fig. 6a shows a main peak for phenyl ethyl phenol and its front shoulder, which corresponds to dibenzothiophenes (DBT) and

naphthothiophene (NT). Here again the OSC peak is less intense comparing to the other co-eluting compounds (Fig. 6a and b). Extracting only the DBT characteristic 184 ion, results in three chromatographic peaks in the color plot, as can be seen in Fig. 6c. This same ion is also characteristic of NT, which has three isomers: naphtho[2,1-b]thiophene (N21bT) naphtho[1,2-b]thiophene (N12bT) and naphtho[2,3-b]thiophene (N23bT).

According to Depauw and Froment [34], there are co-elution problems of these sulphur compounds in 1D-GC using a 100% polydimethylsiloxane column: DBT co-elutes with N12bT; and N21bT co-elutes with phenanthrene. Andersson and Schmid [10] recorded similar problems, which are more pronounced in a 5% phenyl stationary phase, and minimized in a 30% biphenyl phase. According to these authors, the use of a cyanopropyl column can provide separation of these sulphur compounds among themselves and from matrix interferents. However, problems may occur when samples are complex, resulting in a more intense retention of DBT and/or N12bT. Moreover, as previously mentioned, the upper temperature limit of cyanopropyl stationary phase is below 250 °C, which makes analysis of higher molecular sulphur compounds more difficult.

In Fig. 6, the elution order in ^{1}D was N12bT and/or N21bT, N23bT and DBT, which is consistent with the retention data found in the literature for this stationary phase [10] and also for a 100% polydimethylsiloxane [34]. According to Mössner and Wise [35], it was possible to separate the four components (DBT, N12bT, N21bT, N23bT) using a 50% phenyl–50% polydimethylsiloxane or a liquid crystal stationary phase. The analysis of pyrolysed coal showed that it was not possible to separate DBT from N12bT in ^{2}D, although the other compounds were separated (N21bT and N23bT). The mass spectra of both NT and DBT are quite similar and, therefore, whenever co-elution occurs, more analytical information is needed to tentatively identify these compounds. Co-elution of N21bT with phenanthrene in the 5% phenyl–95% dimethylpolysiloxane stationary phase [32] does not occur in GC × GC analysis, as they are resolved in ^{1}D.

Methyl dibenzothiophene (C1-DBT) co-elutes with trimethyl-propenyl naphthalene in 1D-GC and is separated by GC × GC, which is similar to what was observed in the case of C1-BT. Selecting the characteristic ion of DBT and C1-methyl-naphthothiophenes (C1-NT), *m/z* 198, five sulphur compounds difficult to separate were resolved and identified by their mass spectra (figure not shown) [33].

The number of isomers of C1-DBT and C1-NT is 4 and 24, respectively. Depauw and Froment [34] reported co-elution problems between 2-MeDBT and 3-MeDBT in a 100% polydimethylsiloxane column and their separation in a cyanopropyl column. In another study, Mössner and Wise [35] were able to separate this same pair of C1-DBT using a column containing 50% of phenyl groups, although a column with 5% of phenyl groups could not provide separation. The result obtained in this work is in agreement with the litera-
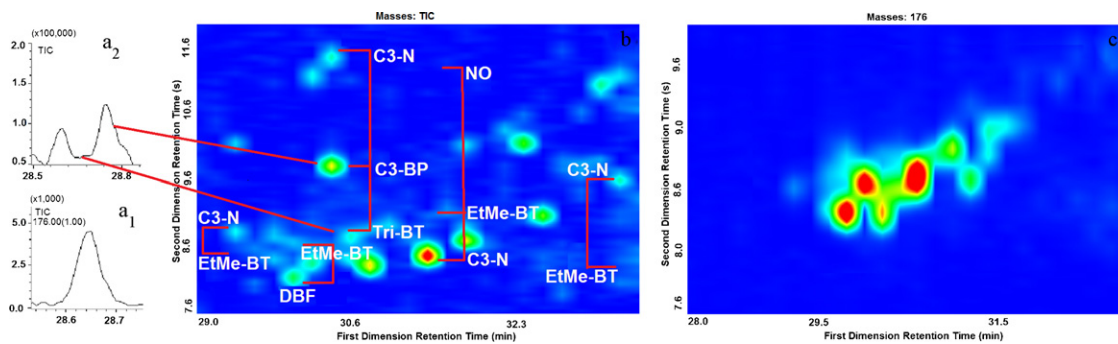
Fig. 5. Total ion current chromatogram for 1D-GC (a_1) extracted ion current chromatogram (a_2), and GC × GC diagram for the region of benzothiophenes with three methyl groups (C3-BT), showing co-elutions of (b) trimethyl naphthalene (C3-N) with ethyl methyl benzothiophene (EtMe-BT); ethyl methyl benzothiophene (EtMe-BT) with dibenzofuran (DBF); trimethyl naphthalene (C3-N); trimethyl-biphenyl (C3-BP) and trimethyl benzothiophene (TriBT); naphthalenol (NO) ethyl methyl benzothiophene (EtMe-BT); and trimethyl naphthalene (C3-N); C3-N and EtMe-BT. (c) GC × GC color plot of the characteristic m/z 176.
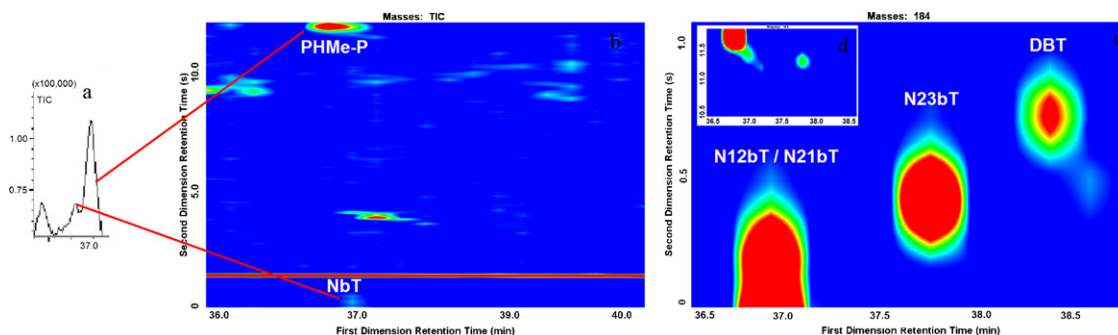

Fig. 6. Total ion current chromatogram for 1D-GC (a), GC × GC diagram (b) for the region of dibenzothiophenes (DBT), indicating co-elutions of DBT with phenylmethyl phenol (PHMe-P). (c) For GC × GC color plot of the characteristic ion m/z 184. Naphtho[1,2-b]thiophene/naphtho[2,1-b]thiophene (N12bT/N21bT), naphtha[2,3-b]thiophene (N23bT), and DBT are shown. (d) Wrap around of one of the chromatographic peaks is presented.

ture, as it was possible to separate this pair of compounds in ^{2}D (50% phenyl). Yet, in another region of the chromatogram, a compound identified as thioxanthene was found when the same ion (m/z 198) was selected.

Mass spectra of dimethyl DBT (C2-DBT) (m/z 212) presented low quality in 1D-GC, as chromatographic peaks of these compounds were of low intensity. GC × GC analysis of the same sample revealed six sulphur compounds. The number of isomers possible is 20 for C2-DBT, 16 for dimethyl-DBT (Di-DBT) and 4 for ethyl dimethyl-DBT (Et-DBT). According to Depauw and Froment [34], it is possible to differentiate between mass spectra of Et-DBT and DiMe-DBT; as fragment m/z 197 is more abundant than the m/z 211 for DiMe-DBT. Based on these considerations, it can be stated that the six sulphur compounds present in this sample are not Et-DBT. However, the mass spectra of DiMe-DBT and DiMe-NT are very similar and cannot be distinguished. Therefore, these compounds may be DiMe-DBT or DiMe-NT. Mössner and Wise [35] used columns with different retention mechanisms and observed co-elution of several of these compounds in a 5% phenyl column and their separation in a 50% phenyl stationary phase.

Results obtained using 1D-GC in the single ion monitoring (SIM) and scan mode revealed no significant differences in the number of peaks detected, except for DBT and NT (characteristic ion is 184) and C2-DBT (characteristic ion is 212). Using 184 ion in the SIM mode of 1D-GC, 6 peaks of DBT and NT were detected (Fig. 7). This indicates that the use of SIM mode only, for a coal tar matrix (or other complex matrices) can eventually lead to misidentification of these compounds, since there are only four possible compounds for the m/z 184 (1 DBT and 3 NT). For C2-DBT twenty peaks were possible and twenty three were detected (figure not shown) with 212 ion. Once again, GC × GC proves its superior separation power
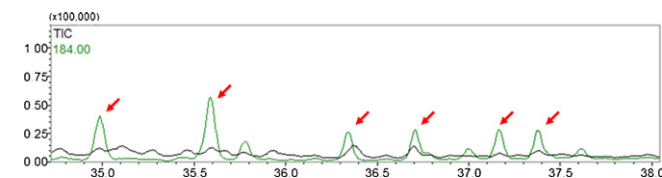
Fig. 7. 1D-GC chromatogram in the selective ion monitoring (SIM) mode with 184 as selected ion (green baseline). Arrows indicate peaks with similar fragmentation. Black baseline corresponds to total ionic current signal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and sensitivity for determination of sulphur compounds in coal tar matrix.

4. Conclusions

A detailed qualitative study regarding separation and tentative identification of sulphur compounds in pyrolysed coal tar using GC × GC/TOFMS and GC/qMS was reported for the first time. GC × GC/TOFMS showed superior efficiency when compared to previous works reported in the literature, as it was possible to separate and identify sulphur compounds in coal tar without the need of previous fractionation steps or multiple chromatographic runs with different stationary phases. The use of a comprehensive 2D-column set of DB-5/DB-17 resulted in less laborious and more expedite analytical procedure, as conventional procedures include the use of more than one stationary phase in different chromatographic runs. The higher efficiency of GC × GC/TOFMS also opens the possibility of unveiling the presence of compounds that were not

yet found in already studied matrix, such as thioxanthene in coal pyrolysate.

Co-elutions among several isomers of sulphur compounds and among these analytes and matrix components were reported for the first time, such as trimethyl thiophene with phenol, and other such cases. The classic analytical challenge of separating chromatographic peaks of PASH and PAH was solved by GC×GC in several cases where 1D-GC provided no resolution. The lack of separation of compounds presenting the same characteristic ion, which can be counted as the same compound in 1D-GC quantitative analysis, was also addressed by GC×GC, as is the case of TriMN and C4–BT.

Another important aspect is that, in some cases, the most commonly used method for sulphur components detection and quantification (1D-GC, SIM mode) can lead to misidentification and overestimation of sulphur compounds content, as a higher and not feasible number of sulphur isomers was found through SIM mode by 1D-GC/qMS. In these cases, GC×GC/TOFMS provided precise information according to what could be expected in relation to the possible number of sulphur isomers.

Acknowledgements

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