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Analysis of Organic Sulphur Compounds in Coal Tar by Using Comprehensive Two-Dimensional Gas Chromatography-High Resolution Time-of-Flight Mass Spectrometry

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Abstract: Coal tar is a complex mixture of organic compounds obtained from the thermal treatment of coal; it contains several different chemical classes of compounds, such as polycyclic aromatic hydrocarbons, phenols and different heterocyclic compounds including sulphur derivatives. In the present research, a target analysis was carried out for the characterisation of fourteen different classes of organic sulphur compounds in coal tar by using cryogenically-modulated (CM) comprehensive two-dimensional gas chromatography-high resolution time-of-flight mass spectrometry (GC×GC-HR ToFMS) with the support of target analyte finding, a specific software function. Furthermore, absolute quantification data were obtained by using eight pure standard sulphur compounds, and 1-fluoronaphthalene as internal standard. Several figures-of-merit of the proposed method were measured (linearity, intra-day precision, limits of detection and quantification). Finally, the overall analytical performance of CM GC×GC-HR ToFMS was evaluated, in relation to MS similarities, mass accuracies, second-dimension peak widths, peak capacity and tailing factors. The approach proved itself as being a powerful analytical platform, benefiting from the high sensitivity, selectivity and resolving power, of both the GC and MS sides.

Keywords: comprehensive two-dimensional gas chromatography; high resolution time-of-flight mass spectrometry; coal tar; organic sulphur compounds

1. Introduction

The concept of comprehensive two-dimensional gas chromatography (GC×GC) was introduced in the early 1990s by Liu and Phillips [1], bringing a great evolution to the GC field. In 1999, the first research work regarding the combination of GC×GC with mass spectrometry appeared [2]. Considering that GC×GC is an established methodology, technical aspects will not be herein addressed. The reader is directed to the literature for more details [3–8].

Coal tar is an extremely complex mixture of organic compounds, obtained as a by-product from the process of coal carbonisation [9]; it is a high-viscosity liquid with a strong odour. Main compounds

are polycyclic aromatic hydrocarbons (PAHs) and derivatives [9]. Other classes of compounds present are: linear, branched, and cyclic hydrocarbons along with heterocyclic compounds containing sulphur [sulphur aromatic heterocycles (SAHs)], oxygen and nitrogen. The interest towards organic sulphur compounds (OSCs) is related to their negative effects on the environment and human health. While the desulphurisation of inorganic species is achievable with physical and chemical methods, the same procedure has proven to be difficult for OSCs [10].

A series of GC×GC-based studies have been published during the last decade, dealing with the characterisation of coal tar, with particular attention devoted to sulphur compounds. For example, a detailed qualitative study of coal tar SAHs was published by Machado et al. [11]. One of the main objectives of the work was to make a direct comparison between gas chromatography-single quadrupole mass spectrometry (GC-QMS) and GC×GC coupled with low resolution time-of-flight mass spectrometry (LR ToFMS). The authors demonstrated that the use of GC×GC-LR ToFMS enabled the identification of a greater number of compounds and also the separation of some SAHs from PAHs, which coeluted completely in the GC-QMS experiment.

In a further research work, Zoccali et al. used the on-line combination of liquid chromatography with GC×GC-triple quadrupole (QqQ) MS, in a proof-of-principle study, for the in-depth analysis of coal tar [12]. Specifically, the use of a normal-phase LC column allowed the separation of three different fractions of coal tar compounds [non-aromatic hydrocarbons, unsaturated compounds (with and without S), and oxygenated constituents], each subjected to GC×GC-QqQMS analysis.

The investigation of OSCs has always evoked interest in the petrochemical field. For this reason, the development of efficient analytical methods for the observation of OSCs in petroleum products is very important. Different strategies based on gas chromatography have been applied to reach such an objective: i.e., pre-fractionation prior to analysis [13], or the use of selective detectors [14]. The separation power of GC×GC has proven to be a good choice, even though issues related to coelution and ions in common between PAH and SAH derivatives have been observed [11,12,15,16]. The use of time-of-flight mass spectrometry, in addition to giving structural information, can provide clean mass spectra for coeluting peaks, via mass spectral deconvolution [4,17].

In general, the combination of GC×GC with high resolution (HR) ToFMS is not so common, compared to other forms of mass spectrometry. During the period between 2014 and 2017, just 8% of the research works involved the use of this combination. Instead, LR ToFMS was by far the most popular choice (66%), followed by QMS (20%) [7].

In 2015, Tranchida et al. developed a flow-modulated GC×GC-HR ToFMS method for the untargeted and targeted analysis of OSCs in heavy gas oil. The main focus of the study was the coupling of flow-modulated GC×GC with HR ToFMS [16]. In a further GC×GC-HR ToFMS study, Byer et al. highlighted the MS capability to distinguish between compounds characterised by an elemental composition difference of C3 vs. SH4 in a sample of crude oil [18].

The main objective of the present study was to characterise different classes of OSCs in coal tar by using GC×GC-HR ToFMS. Altogether, fourteen chemical classes were targeted through the use of the target analyte finding (TAF) data processing method. The absolute quantification of a series of OSCs was also performed. The overall analytical performance of GC×GC-HR ToFMS was evaluated, proving it to be a very powerful analytical platform. To the best of the present Authors' knowledge, there have been no studies regarding the investigation of OSCs in coal tar by using GC×GC-HR ToFMS.

2. Materials and Methods

2.1. Samples, Standard Compounds and Reagents

The sample of coal tar derived from the Cabuí coal field (Figueira, Paraná, Brazil). The sample was diluted in dichloromethane to a final concentration of 100 mg L⁻¹. Eight pure standard compounds, namely (the chemical class abbreviation is reported in parenthesis, with C1, C2, etc., related to the number of carbons in the alkyl substituents): 3-methylthiophene (C1-T),

2,5-dimethylthiophene (C2-T), 2-propylthiophene (C3-T), 3-butylthiophene (C4-T), benzo[b]thiophene (BT), 2-methylbenzo[b]thiophene (C1-BT), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (C2-DBT), and the internal standard, (IS) 1-fluoronaphthalene, were purchased from Merck Life Science (Merck KGaA, Darmstadt, Germany). The standards were solubilised in dichloromethane at eight final concentrations, across two orders of magnitude (see Section 3.3). In each calibration solution, and in the diluted coal tar, the IS was present at a concentration of $89 \mu\text{g L}^{-1}$.

2.2. Instrumental Conditions

The GC×GC-HR ToFMS applications were performed on a Pegasus GC-HRT 4D system (LECO, Mönchengladbach, Germany). The following set of columns was used: an apolar first-dimension (¹D) column, namely SLB-5ms, [equivalent in polarity to poly(5% diphenyl/95% dimethyl siloxane)] with dimensions $30 \text{ m} \times 0.25 \text{ mm ID} \times 0.25 \mu\text{m } d_f$ and an intermediate polarity second-dimension (²D) one, namely an SLB-35ms, with dimensions $1.9 \text{ m} \times 0.10 \text{ mm ID} \times 0.10 \mu\text{m } d_f$ [equivalent in polarity to poly(35% diphenyl/65% dimethyl siloxane)], with 0.7 m inside the MS transfer line. The connection between the columns was made through the use of a Siltite mini union (Trajan, Ringwood, Victoria, Australia). Modulation was achieved by using a consumable-free quad-jet cryogenic modulator, using the first 10 cm of the second analytical column as modulation capillary. The carrier gas was He and was used under a constant flow of 1 mL min^{-1} . The system was equipped with a split/splitless injector ($300 \text{ }^\circ\text{C}$), while the injection volume was $2 \mu\text{L}$ (split ratio was 5:1). The temperature program was 50 to $300 \text{ }^\circ\text{C}$ at $6 \text{ }^\circ\text{C min}^{-1}$ with a secondary oven offset of $+5 \text{ }^\circ\text{C}$. Transfer line temperature: $300 \text{ }^\circ\text{C}$. The modulation period was set at 3.5 s: the hot jet was held for 0.3 s, and the cold jet for 1.45 s until 28 min; afterwards, the duration of the jets was reversed in order to allow the release of high boiling point compounds. Modulation heating temperature: $+15 \text{ }^\circ\text{C}$ offset with respect to the temperature of the main GC oven; modulation cooling temperature: $-90 \text{ }^\circ\text{C}$.

The ²D eluate was monitored by the HR ToFMS instrument by using electron ionisation (70 eV), at a source temperature of $250 \text{ }^\circ\text{C}$, and a mass range of 45–450 amu. The high resolution mode was used (25,000 full width half maximum—fwhm) with a spectral production frequency of 200 Hz. Analysis data were acquired and processed by using the LECO ChromaToF-HRT software (v. 5.20.36). Mass spectral matching was performed by using the NIST 2017 Mass Spectral Library and an in-lab-constructed high resolution MS OSC database. Other parameters regarding the data processing method are reported as supplementary material (Table S1).

3. Results and Discussion

3.1. Instrumental Aspects and Performance

A pure standard solution of eight SAHs (100 ppb), plus the IS (89 ppb), was first analysed to evaluate various parameters concerning the instrumental performance. Peaks widths [at the base (w_b) and at half height (w_h)], ²D peak capacity, tailing factors (TFs), mass accuracies, and HR ToFMS similarities were measured. Such features were calculated by performing ten consecutive analyses of the pure standard solution.

The GC method was characterised by a duration of approx. 41.7 min and a linear temperature gradient with a secondary oven offset of $+5 \text{ }^\circ\text{C}$. The ¹D gas linear velocity was approx. 11 cm s^{-1} and 15 cm s^{-1} (void-time: ≈ 270 and 200 s), at the beginning and at the end of the analysis, respectively. The ²D gas linear velocity was approx. 85 cm s^{-1} and 127 cm s^{-1} (void-time: ≈ 1.8 and 1.3 s) at the beginning and at the end of the analysis, respectively. The average peak widths were 106 ms (w_b) and 62 ms (w_h). The peak capacity, calculated using the w_b value, was approx. 33. Furthermore, a TF average value of 1.1 was determined: the lowest TF value was 0.8 for 2-propylthiophene, while the highest one was 1.9 for 3-methylthiophene.

The acquisition frequency of the HR ToFMS system (200 Hz), in relation to the peak widths, was sufficient for the purposes of reliable quantification and deconvolution [17,19]. In fact, for optimum

deconvolution in particular, 12 data points across the peak width at half height are required [20]. The average mass accuracy error values expressed in ppm, relative to the molecular ions, were in the range 0.4–4.6 ppm and are listed in Table 1. It is noteworthy that such values are absolute ones because negative mass error values were always considered as positive. With regards to the MS similarity, an average value of 930 was calculated, with a range between 901 and 954.

Table 1. Pure standard compounds, first and second dimension retention times (t_R), molecular formula, theoretical $[M]^{+\bullet}$ m/z value, average mass accuracy error, and HR ToFMS database similarity.

Compound	1D t_R (min)	2D t_R (sec)	Formula	Theor. $[M]^{+\bullet}$	Average Error (ppm)	Match
3-Methylthiophene	8.0	2.0	C ₅ H ₆ S	98.018473	1.2	954
2,5-Dimethylthiophene	9.7	2.1	C ₆ H ₈ S	112.034123	0.4	901
2-Propylthiophene	11.5	2.1	C ₇ H ₁₀ S	126.049773	0.5	906
3-Butylthiophene	14.4	2.3	C ₈ H ₁₂ S	140.065423	0.6	935
1-Fluoronaphthalene (IS)	17.4	2.6	C ₁₀ H ₇ F	146.052630	1.0	942
Benzo[b]thiophene	17.6	2.7	C ₈ H ₆ S	134.018473	0.5	937
2-Methylbenzo[b]thiophene	20.2	2.7	C ₉ H ₈ S	148.034123	2.7	928
Dibenzothiophene	29.3	3.5	C ₁₂ H ₈ S	184.034123	3.7	917
4,6-Dimethyldibenzothiophene	32.5	3.7	C ₁₄ H ₁₂ S	212.065423	4.6	954

3.2. Target Analysis

The combination of CM GC×GC with HR ToFMS allows the performance of both targeted and untargeted analysis. A main objective of the investigation was the pre-targeted analysis of classes of OSCs; an automatic data processing method—TAF—was developed. This software function enables users to look for a set of selected analytes without the need for a full peak finding process. For the eight standard compound classes, information related to retention times (1D t_R : ± 2 min; 2D t_R : ± 0.3 s) and significant ions with a minimum level of mass accuracy (± 10 ppm allowance) was derived from the analyses of the standard compounds. For other six classes, the MS information was acquired from the literature [11], and through a preliminary investigation of the GC×GC-HR ToFMS result on the coal tar sample. No retention time window for these additional compounds was used during the TAF process. The $^1D \pm 2$ min time window was selected to cover the chemical classes with a higher number of positional isomers. The theoretical accurate mass fragments used for the TAF process are reported in Table 2.

Through the applied method, 60 sulphur compounds belonging to 14 different classes were detected. The class with the highest number of compounds was C3-BT (13) followed by C4-BT and C2-DBT (9). The total-ion current (TIC) bidimensional plot of the coal tar sample is shown in Figure 1. The analyte distribution, on the apolar-mid polarity column combination, is rather typical for a petrochemical sample (the chemical classes are highlighted). The presence of two solvent bands is evident in the chromatogram. This effect is probably due to non-efficient entrapment of dichloromethane (b.p. ≈ 40 °C) during modulation.

A software designated analytical ion chromatogram (AIC) was generated, enabling the visualisation of the 14 chemical classes (plus the IS) involved in the present study (Figure 2). The high selectivity of the method developed is clearly visible in the AIC, with each OSC group confined in a specific region of the chromatogram. The selectivity achieved is comparable to that of the sulphur chemiluminescence detector [14], though accompanied by the structural information provided by HR ToFMS.

Table 2. Chemical classes, first and second dimension retention times, characteristic ion for the OSCs used for the TAF method and the base peak ion (all theoretical masses) for the coeluting compounds. Chemical class abbreviations: B = Benzene; N = Naphthalene; P = Phenanthrene; A = Anthracene; NT = Naphthothiophene.

Class	¹ D t _R (min)	² D t _R (sec)	TAF Ion	Coeluting Class and Base Peak
C1-Thiophene	8.0	2.0	97.010648	
C1-T	8.1	2.0		
C2-Thiophene	10.0	2.1	111.026298	
C2-T	10.3	2.1		
C3-Thiophene	11.8	2.2	97.010648	105.069877 (C3-B)
C3-T	11.9	2.1		
C3-T *	12.2	2.2		
C3-T	12.5	2.2		
C4-Thiophene	14.2	2.2	97.010648	105.069877 (C4-B)
C4-T	14.4	2.2		
C4-T	14.7	2.3		
Benzo[b]thiophene	17.9	2.7	134.018473	
C1-Benzothiophene	20.1	2.7	147.026298	142.077702 (C1-N)
C1-BT *	20.3	2.7		
C1-BT	20.5	2.8		
C1-BT *	20.6	2.8		
C2-Benzothiophene	22.3	2.8	161.051948	156.093352 (C2-N)
C2-BT *	22.4	2.8		
C2-BT *	22.7	2.8		
C2-BT *	22.8	2.8		
C2-BT *	23.0	2.8		
C3-Benzothiophene	24.1	2.8	161.051948	155.085527 (C3-N)
C3-BT	24.3	2.8		
C3-BT	24.4	3.0		
C3-BT	24.5	2.8		
C3-BT *	24.7	2.8		
C3-BT	24.8	2.8		
C3-BT *	25.0	2.8		
C3-BT	25.1	2.8		
C3-BT *	25.2	2.9		
C3-BT	25.3	2.9		
C3-BT	25.5	2.8		
C3-BT *	25.6	2.9		
C3-BT	25.7	2.9		
C4-Benzothiophene	26.1	2.8	175.057598	
C4-BT	26.2	2.8		
C4-BT	26.5	2.8		
C4-BT	26.6	2.8		
C4-BT	26.7	2.8		
C4-BT	27.0	2.9		
C4-BT	27.3	2.9		
C4-BT	27.5	2.9		
C4-BT	27.7	3.0		
Dibenzothiophene	29.6	3.5	184.034123	
Naphthothiophene *	30.1	3.6	184.034123	178.077702 (P)
NT	30.6	3.7		
C1-Dibenzothiophene	31.3	3.5	198.049773	
C1-DBT	31.4	3.6		
C1-DBT	31.6	3.6		
C1-DBT	31.8	3.6		
Thioxanthene *	31.9	3.7	198.049773	192.093352 (C1-A)
C2-Dibenzothiophene	32.8	3.7	212.065423	
C2-DBT	33.1	3.7		
C2-DBT	33.5	3.8		
C2-DBT	33.7	3.9		
C2-DBT	34.1	3.9		
C2-DBT	34.1	4.0		
C2-DBT	34.2	4.0		
C2-DBT	34.3	4.0		
C2-DBT	34.4	4.0		

* Coelution.

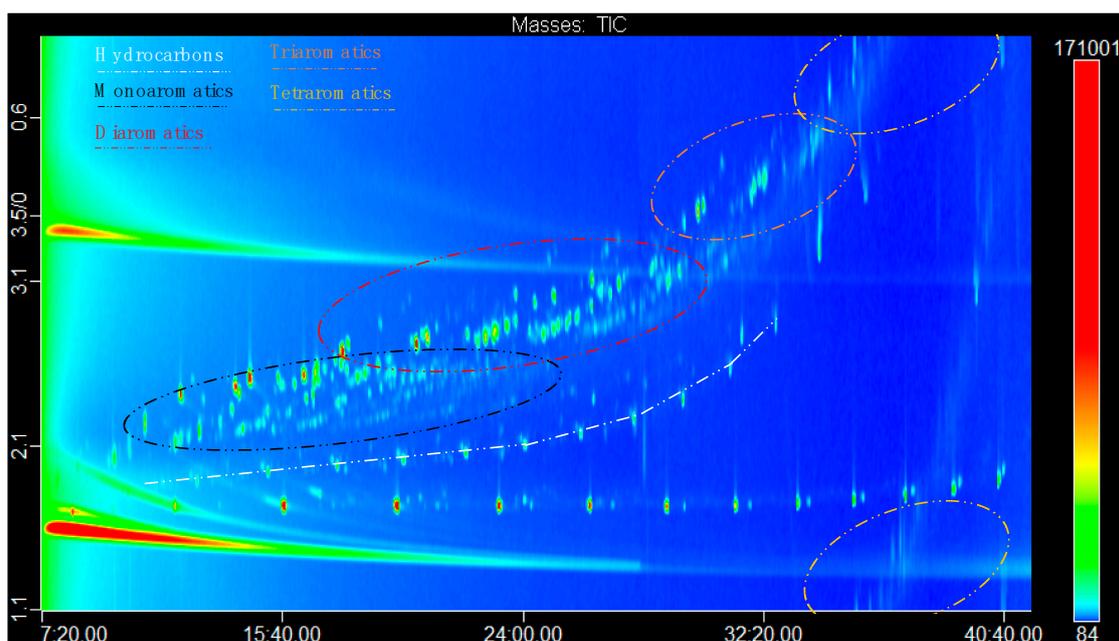


Figure 1. Total ion current GCxGC-HR ToFMS chromatogram of coal tar, highlighting the main chemical classes.

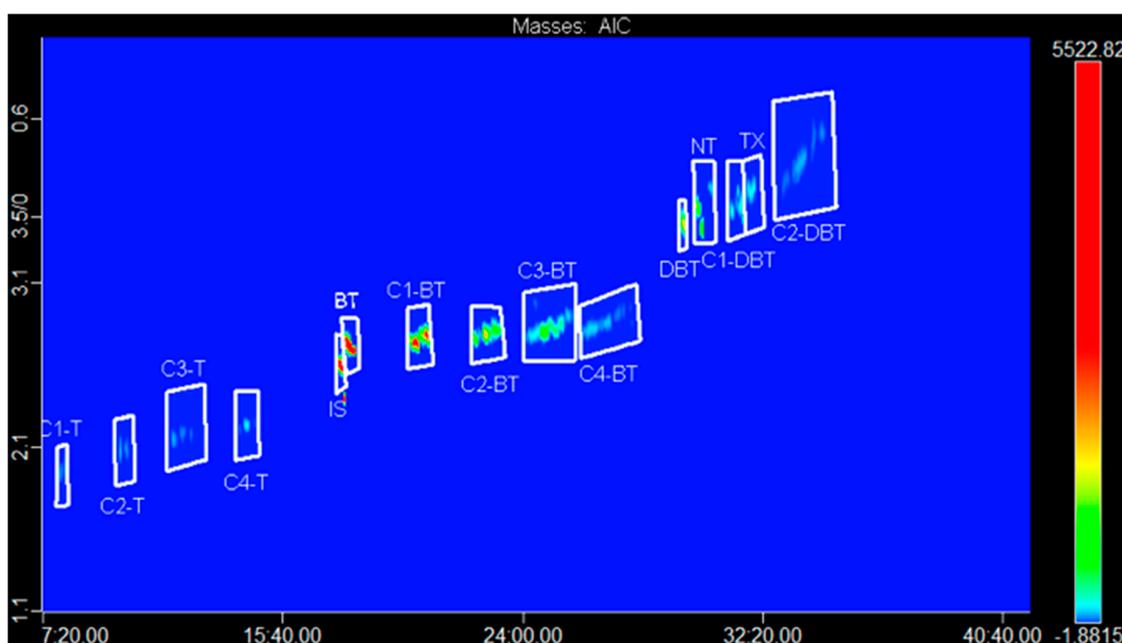


Figure 2. Analytical ion chromatogram showing the OSCs found by the targeted process. Abbreviation: TX = Thioxanthene.

As aforementioned, the possibility of coelutions between SAH and PAH derivatives is a well-known issue [11]. Such an occurrence was investigated for the 14 OSC classes by exploiting the high mass resolution and deconvolution capabilities of the instrument. In general, the degree of coelution observed between SAHs and PAHs in the coal tar TIC trace (Figure 1) reached a value of about 21%, with the majority involving C2-BTs and C2-Ns, and C3-BTs and C3-Ns (Table 2). As an example, the near complete coelution between C1-BT and C1-N compounds, spectrally resolved through the deconvolution process, is illustrated in Figure 3. An extracted ion chromatogram (XIC) expansion is shown in Figure 3a, with the two compounds characterised by a retention time difference of only 20 ms. The deconvoluted

mass spectra of the C1-N (1-methylnaphthalene) and C1-BT (2-methylbenzo[b]thiophene) compounds are shown in Figure 3b,c, respectively: the former compound was tentatively identified with a spectral similarity value of 911 (NIST 2017 Mass Spectral Library), while the latter was characterised by a similarity of 906 (in-lab-constructed database).

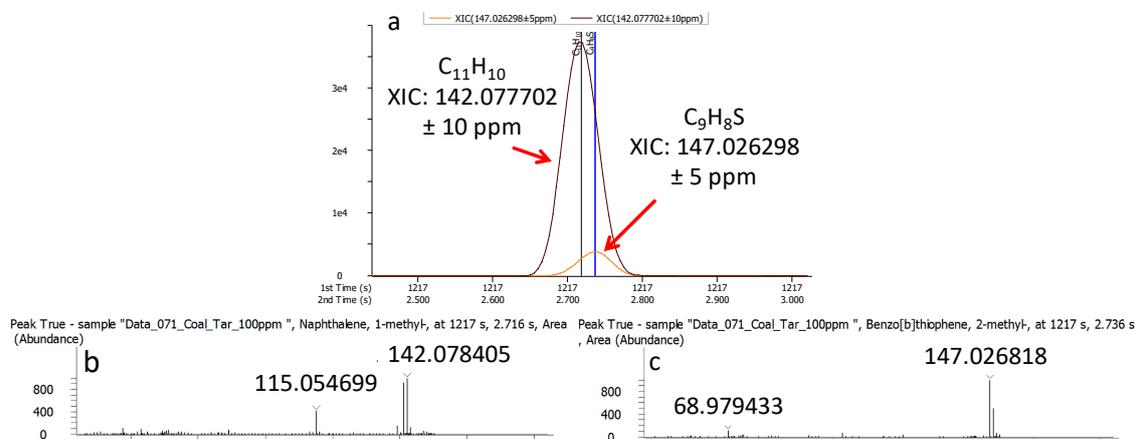


Figure 3. Extracted ion chromatogram expansion highlighting a coelution between C1-BT (spectrally identified as 2-methyl[b]benzothiophene) and C1-N (spectrally identified as 1-methylnaphthalene) (a). Deconvoluted mass spectrum for 1-methylnaphthalene (b) and 2-methyl[b]benzothiophene (c).

3.3. Quantitative Analysis

In order to perform quantitative analysis, eight-point calibration curves across two orders of magnitude were constructed for the eight SAHs. The ppb concentration range for each compound is shown in Table 3, along with the quantifier ion (the base peak). In all cases, the lowest calibration point was approx. at the 5 ppb level, while the upper one was approx. at the 500 ppb level. The internal standard (1-fluoronaphthalene) was added to all solutions at a concentration of 89 $\mu\text{g L}^{-1}$. Eight replicates were carried out at the three lowest points, while six consecutive analyses were performed for the other concentrations. Coefficients of determination were in the range 0.97414–0.98941. The quantifier ions, along with the average mass error values (range: 1.0–3.4 ppm), for the eight SAHs as well as for the IS, are also reported. Limits of detection (LoD) and quantification (LoQ) values were calculated by dividing the standard deviation of the response at the lowest calibration point by the equation slope, and then by multiplying the result by 3 and 10, respectively. Finally, the LoDs and LoQs were adjusted by considering the initial sample dilution (100 mg L^{-1}), and were in the range 5.0 (2,5-dimethylthiophene)–30.0 (3-methylthiophene) mg L^{-1} and 17.0 (2,5-dimethylthiophene)–110.0 (3-methylthiophene) mg L^{-1} , respectively. Intra-day precision, expressed as relative standard deviation (RSD), and calculated for the 100 $\mu\text{g L}^{-1}$ calibration point (comprising the IS), was between 1% and 4%, demonstrating satisfactory repeatability (Table 3).

Table 3. Pure standard compounds, quantifier ions, average mass accuracy errors, calibration ranges, coefficients of determination (R^2), coal tar SAH concentrations, LoDs, LoQs, and RSDs.

Compound	Quantifier	Average Error (ppm)	Range (ppb)	R^2	Coal Tar (mg L^{-1})	LoD (mg L^{-1})	LoQ (mg L^{-1})	RSD (%)
3-Methylthiophene	97.010648	2.5	5.0–500	0.98941	>LoD	30.0	110.0	2
2,5-Dimethylthiophene	111.026298	2.5	5.8–580	0.98908	87.6	5.0	17.0	4
2-Propylthiophene	97.010648	3.4	5.2–520	0.98819	>LoD	7.0	25.0	2
3-Butylthiophene	97.010648	2.8	5.2–525	0.98876	>LoD	7.0	23.0	2
1-Fluoronaphthalene (IS)	146.052630	1.0						2
Benzo[b]thiophene	134.018473	2.0	5.5–555	0.97414	1516.8	6.0	20.0	1
2-Methylbenzo[b]thiophene	147.026298	1.7	5.0–500	0.98723	767.4	10.0	35.0	1
Dibenzothiophene	184.034123	2.6	5.1–510	0.98630	599.7	9.0	30.0	2
4,6-Dimethyldibenzothiophene	212.065423	3.4	5.1–515	0.98882	>LoD	8.0	28.0	4

The coal tar sample, spiked with the IS, was analysed three times consecutively; benzo[b]thiophene was the most abundant compound (1516.8 mg L⁻¹), followed by 2-methylbenzo[b]thiophene and dibenzothiophene (767.4 and 599.7 mg L⁻¹, respectively). Admittedly, the calculated concentration of benzo[b]thiophene was rather far from the upper calibration point (555 ppb). Four other compounds were detected (3-methylthiophene, 2-propylthiophene, 3-butylthiophene, 4,6-dimethyldibenzothiophene), though at concentrations below the LoQ. As can be seen, the range of SAH concentrations in coal tar was rather wide, meaning that the initial sample dilution can be regulated for compounds that are far above the upper calibration point or below the LoQ.

4. Conclusions

A CM GC×GC-HR ToFMS approach for the targeted analysis of OSCs in a coal tar sample has been developed. The overall analytical performance related to the method, in its various aspects, can be considered as satisfactory. The method herein proposed allowed the pinpointing of 60 OSCs, belonging to 14 different classes.

Absolute quantitative information was obtained for 8 SAHs, which can provide a good albeit approximate idea on the concentration of each chemical class in the petrochemical sample under investigation. Moreover, the initial dilution of the sample can be adjusted for OSCs quantified at excessively high concentration levels or below the LoQ.

Further research will be devoted to the expansion of the sulphur chemical classes investigated using the TAF approach and to the absolute quantification of additional OSCs representative of specific chemical classes.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2297-8739/7/2/26/s1>, Table S1: ChromaToF-HRT software data processing parameters.

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