New Developments in Mass Spectrometry for Group-Type Analysis of Petroleum Cuts (Second Part)

A. Fafet, J. Bonnard, F. Prigent

HAL Id: hal-02075820

https://hal-ifp.archives-ouvertes.fr/hal-02075820

Submitted on 21 Mar 2019

New Developments in Mass Spectrometry for Group-Type Analysis of Petroleum Cuts

First Part: Improving Quantification of Sulphured Aromatic Compounds in Middle Distillates

A. Fafet[1], J. Bonnard[1], F. Prigent[1]

1 Institut français du pétrole, 1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
e-mail: anne.fafet@ifp.fr

INTRODUCTION

Detailed characterization of petroleum cuts constitutes a necessary step to perfect understanding of the reaction mechanisms and to the description of the kinetics of certain refining processes such as hydrotreating or catalytic cracking. But, except for gasoline, which can be characterized on a molecular basis thanks to gas phase chromatography [1], it is impossible to obtain complete description of the other cuts such as middle distillates and vacuum distillates. Few analytical techniques enable to access this quantitative information taking into account the complexity of the mixtures to be studied (several thousand compounds).

For many years, methods using mass spectrometry (MS) have allowed very detailed group-type analysis, of middle distillates [2-5] as well as of heavy cuts [4, 6-8]. They enable to reach the detail of aliphatic hydrocarbons (alkanes, one to several rings cycloalkanes), aromatic hydrocarbons (monoaromatic (C_nH_{2n-6} to C_nH_{2n-10}), diaromatic (C_nH_{2n-12} to C_nH_{2n-16}), triaromatic and polyaromatic hydrocarbons as well as sulphured and even disulphured aromatic). These methods differ by certain parameters such as the resolution used, the requirement of prior separation or the ions used for quantification.

The main advantage of these direct methods lies in the fact that they are readily implementable and are the only ones to provide with relatively complete description of these petroleum cuts. But these techniques are also subject to some drawbacks and we shall expose, thereunder, two examples of study liable to improve them.

These shortcomings lie mainly in the quantitative calculation matrices of the chemical groups. These matrices have been created taking into consideration a certain fragmentation and a certain relative sensitivity of each compound or group-type. Strict operating conditions are therefore advised. However, certain operating parameters, which cannot be controlled and which are partly due to the ageing of the source, may vary and bring about their modification. One of the means available to adjust these conditions consists in using a test cut whose theoretical composition can be known thanks to other techniques (mainly the saturated hydrocarbons/aromatic hydrocarbons ratio and the sulphur content). Another restriction results from obtaining sensitivity coefficients and intergroup contributions. These are average values obtained correlatively. This means that if statistic distribution within each group, as postulated by the authors, deviates from than of the samples excessively, the result will not be as

accurate. This is the case of very narrow cuts or of pure products. Besides, there are no standard compounds enabling to prove the accuracy of such methods. One of the possibilities in this field consists in performing intertechnique comparisons. Thus, the accuracy of the quantification of sulphured compounds can be checked by comparison with the results obtained by gas phase chromatography coupled to sulphur-specific detection such as chemiluminescence or atomic emission. This study forms the first part of this article.

In a second part (*Rev. IFP*, Vol. 54 (1999) No. 4, pp. 453-462, following in this issue), we shall describe the conception and the validation of a new type of inlet system. Indeed, to be able to analyse samples that are as complex as petroleum cuts, we must be in a position to vaporise them in the source of the spectrometer. For middle distillates, commercial systems are available and enable to introduce the sample in satisfactory conditions. This is far more difficult for heavy cuts, especially if we consider that their initial boiling temperature corresponds to the onset of thermal cracking and that their final boiling point is often higher than 600°C. This constitutes the most crucial element since a very limited number of introduction systems exhibit the required characteristics.

Résumé — **Nouveaux développements en spectrométrie de masse pour l'analyse quantitative par famille chimique des coupes pétrolières** — La caractérisation des coupes pétrolières est une étape indispensable à la compréhension des mécanismes réactionnels et à la description de la cinétique de certains procédés de raffinage comme l'hydrotraitement ou le craquage catalytique. La spectrométrie de masse (SM), grâce aux méthodes d'analyse quantitative par famille, permet d'accéder à une description détaillée des mélanges complexes d'hydrocarbures que sont les distillats moyens ou les coupes lourdes comme les distillats sous vide. Mais ces méthodes présentent certaines limitations et nous exposons ici deux exemples d'amélioration.

Dans une première partie, la justesse de la quantification par SM des composés soufrés thiophéniques dans les distillats moyens est étudiée par comparaison intertechniques avec les résultats obtenus par chromatographie gazeuse couplée à une détection spécifique du soufre par chimiluminescence (CG/SCD). Une amélioration de la méthode SM est proposée.

La seconde partie présente la description d'un nouveau système d'introduction de l'échantillon dans la source du spectromètre, dédié à l'analyse par famille des coupes lourdes. Nous exposons sa validation, par comparaison des résultats de SM avec ceux de la chromatographie liquide (CL), ainsi que ses performances.

Mots-clés : spectrométrie de masse, analyse quantitative par famille, distillats moyens, composés soufrés, chromatographie gazeuse couplée à une détection spécifique par chimiluminescence.

Abstract — New Developments in Mass Spectrometry for Group-Type Analysis of Petroleum Cuts —
Characterization of petroleum cuts constitutes a necessary stage to perfect understanding of the reaction mechanisms and to the description of the kinetics of certain refining processes such as hydrotreating or catalytic cracking. Mass spectrometry (MS), thanks to group-type quantitative analysis methods, enables to access detailed description of complex hydrocarbon mixtures such as middle distillates or heavy cuts such as vacuum distillates. But these methods are also subject to some drawbacks and we shall expose, thereunder, two examples of improvements.

In a first part, the accuracy of MS quantification of thiophenic sulphured compounds in middle distillates is studied by intertechnique comparison with the results obtained by gas phase chromatography coupled to sulphur-specific detection by chemiluminescence (GC/SCD). Improving on the MS method is suggested.

In the second part, a new system for introducing the sample in the spectrometer source, dedicated to group-type analysis of heavy cuts is described. Its validation, by comparison of the MS results to those of liquid chromatography (LC) as well as its performances, is exposed.

Keywords: mass spectrometry, quantitative group-type analysis, middle distillates, sulphured compounds, gas chromatography coupled with specific detection by chemiluminescence.

IMPROVING QUANTIFICATION OF SULPHURED AROMATIC COMPOUNDS IN MIDDLE DISTILLATES

Characterization of middle distillates (kerosenes, gas oils) can be performed by various analytical techniques. Thus, by liquid chromatography, it is possible to separate aliphatic hydrocarbons and aromatic hydrocarbons [9]. HPLC (high performance liquid chromatography) [10, 11] as well as ultraviolet spectrometry [12] enable to access to a greater level of detail while distinguishing within aromatic hydrocarbons, the monoaromatic, diaromatic and polyaromatic compounds. New techniques, such as supercritical chromatography (SFC) are quite promising in this field [13].

By mass spectrometry, the distribution of aliphatic compounds into alkanes, single and multi-cycle cycloalkanes as well as aromatic hydrocarbons into monoaromatic (of raw formula C_nH_{2n-6} to C_nH_{2n-10}), diaromatic (C_nH_{2n-12} to C_nH_{2n-16}), triaromatic and polyaromatic hydrocarbons and sulphured molecules is accessible. Recently, techniques coupling either liquid chromatography and low energy mass spectrometry [14] or gas phase chromatography and chemical ionisation mass spectrometry [15] or gas phase chromatography and classical mass spectrometry [16] have been introduced and they enable fine-tuning of these characterizations while specifying distribution by chemical group-type and by numbers of carbon atoms.

In the field of characterization of sulphured compounds, techniques such as gas phase chromatography coupled with sulphur-specific detectors (chemiluminescence, atomic emission) have provided with additional information on isomerism of these molecules and on their quantification at very low contents [17]. In the same way, GC/MS coupling studies based on specific ion detection mode [18, 19] have enabled to progress in detailed characterization of these compounds.

Direct analysis by group-type and by mass spectrometry still remains the most complete and the fastest implementation technique, while giving in a single measurement relatively detailed description of all the chemical groups in presence in a distillate. But, as mentioned previously, the accuracy of the analyses cannot be checked using standard samples. Only intertechnique comparisons enable in some cases to assess the accuracy of the results on certain groups. For instance, it is quite common to look at the consistency of the data resulting from mass spectrometry and from HPLC for global quantification of mono-, di- and polyaromatic hydrocarbons. The development of alternative methods gives the opportunity to conduct this approach on sulphured compounds.

Our study related more specifically to quantification of sulphured aromatic molecules, benzothiophenes (BT) and dibenzothiophenes (DBT). In this view, the results of mass spectrometry have been set against those of gas phase chromatography coupled to sulphur-specific detection by chemiluminescence (GC/SCD).

1 GENERALS

1.1 Principle and Scope of Mass Spectrometry Quantification

The MS method used consists of an average resolution analysis ($R = 5000$) without any prior separation and is derived from ASTM D2425 [5]. Its scope covers petroleum cuts whose boiling point ranges 180 and 400°C. It does not call for prior separation. It quantifies twelve groups (in % m/m) among which three aliphatic (paraffin, non-condensed naphthenes and condensed two and three ring-naphthenes), seven aromatic (with one to three condensed rings) and two sulphured aromatic compounds. The contribution of each group-type is determined by the sum of the molecular peaks M^+ and/or fragment peaks $(M-H)^+$, weighed by its average response coefficient and corrected by the contribution of the other group-types.

One of its restrictions lies in the interference between sulphured compounds and four-rings polyaromatic compounds. Indeed, when the final boiling point is greater than 350°C, certain polyaromatic compounds containing more than three rings, such as pyrenes, can be present in a quantity detectable by current techniques. The spectra of such molecules exhibit interference with those of sulphured aromatic compounds. They have the same molecular mass nominale and their exact mass is separated from 0.0034 a.m.u. Thus, dihydropyrenes (C_nH_{2n-20}) can be confused with alkylbenzothiophenes ($C_nH_{2n-10}S$). Much higher resolution ($R = 80\,000$) will be necessary to clarify these ambiguities. But these conditions are extreme for most commercial spectrometers and cannot be met conventionally. Besides, sensitivity is so bad that only major compounds can then be detected.

1.2 Principle of Sulphured Compounds Analysis by Gas Phase Chromatography/Sulphur-Specific Detection by Chemiluminescence (GC/SCD)

The compounds of the mixture are separated by the chromatographic column and burnt in a flame ionising detector. The released gases are directed to an ozonolysis cell. The oxidation products resulting from sulphured compounds (SO_2, SO, etc.) react to the ozone and are then chemiluminescent. The radiation is captured by a photomultiplier. This detector provides with a chromatogram where only sulphured molecules have reacted. It exhibits the particularity of being very sensitive and especially very selective with respect to co-eluent hydrocarbons. Its response is linear over a wide range, equimolar and independent from the structure of the sulphured compound. The advantage of this technique, for the analysis of middle distillates, lies in its capacity to dose quantitatively (in %m/m) and individually certain sulphured molecules, each of which exhibits a clearly cut peak.

In the case of middle distillates resulting from catalytic cracking (light cycle oil (LCO)) that contains essentially thiophenic compounds, the chromatogram is simple and of relatively good resolution. It is possible to distinguish certain molecules such as benzothiophene and its alkylated forms up to four carbon atoms and dibenzothiophene and several of its alkylated forms (Fig. 1). Quantification of each of these species can be carried out while calculating the area percentage of each of these peaks. As the detector reacts in % m/m of sulphur, it is possible, by knowing the molecular mass associated with each peak, to calculate the % m/m of each sulphured molecule. Taking into consideration that all the eluted compounds before DBT are alkylated BT (BTs) and that all eluted from the DBT are alkylated DBT (DBTs), the global ratio of BTs and of DBTs can be determined [17].

In the case of middle distillates derived from direct distillation (straight-run, SR), a non-resolved signal appears (Fig. 2). It is due to the other forms of sulphured compounds, such as sulfides and mercaptans. It becomes then impossible to quantify each species correctly. This constitutes the main restriction of the method for quantitative characterization of middle distillates. The scope is limited to the cuts whose heaviest compounds can be eluted from the chromatographic column. On the column used for our tests, the accepted final boiling point is close to 450°C (C_{30}).

2 EXPERIMENTAL PART

2.1 Samples

Eight middle distillates resulting from the catalytic cracking process (LCO and HCO (high cycle oil)) have been used for this study. Their characteristics are given in the Table 4. The sulphur content ranges from 0.3 to 2% m/m and the T_{50} (temperature where 50% m/m of the product has been distillated) from 260°C to 350°C.

2.2 Mass Spectrometry

This development has been accomplished by a high-resolution spectrometer Ultima manufactured by *Fisons*. The sample is introduced via a batch inlet system heated to 250°C ± 5°C. Analysis is performed by electronic impact at 70 eV and at middle resolution ($R = 5000$) in order to differentiate ions of identical nominale mass, but belonging to different groups. Some ten spectra (all representative of the mixture) can be acquired at 3 s/decade with a 30-350 a.m.u. mass range. They are averaged in order to improve the signal/noise ratio. The source is tuned in order to get maximum sensitivity and validated thanks to the analysis of a standard distillate whose saturated/aromatic compounds ratio is known by liquid chromatography.

2.3 Gas Phase Chromatography/Sulphur-Specific Detection by Chemiluminescence (GC/SCD)

The chromatograph is a HP5890, fitted with a 350B Sievers detector. The column is a 30 m ∞ 0.32 mm ID SPB-1 with a 4 µm film. The temperature program is as follows: 60 (5 min) at 280°C (40 min) at 5°C/min. The carrier gas is helium. On-column injection is used and the injector is programmed from 90 to 280°C at 200°C/min. The detector is set at 280°C. The gas flow rates are: H_2 200 ml/min, air: 400 ml/min and makeup: 20 ml/min.
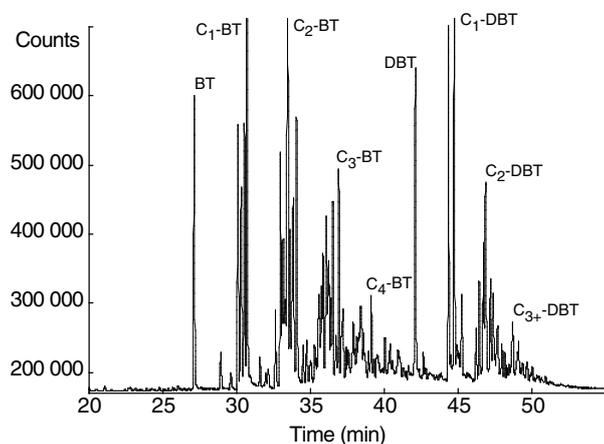

Figure 1

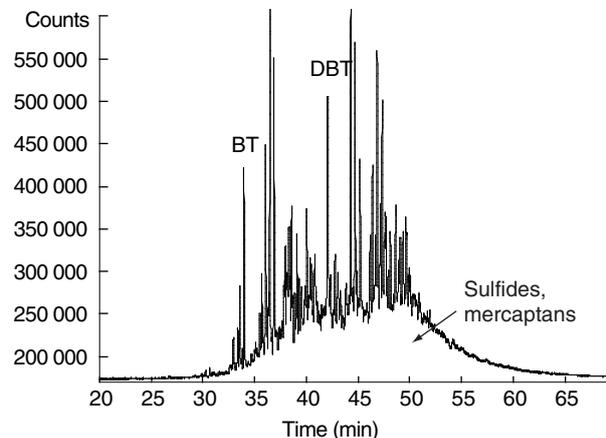GC/SCD chromatogram of a distillate derived from catalytic cracking (LCO).

Figure 2

GC/SCD chromatogram of a middle distillate derived from direct distillation (straight run).

3 RESULTS AND DISCUSSION

3.1 MS/SDC Comparison

Validating any method by intertechnique comparison is based upon the selection of a reference method and of a set of samples representative of the field of application. Taking into account the chromatographic restrictions mentioned in the previous paragraph, the GC/SCD brings results that can be considered as the best estimate of concentrations of sulphured groups, only in the case of distillates containing thiophenic groups exclusively: distillates derived from catalytic cracking or hydrotreating processes.

This is the reason why MS/SDC comparison was conducted on eight middle distillates derived from FCC (LCO and HCO), whereas the deviations observed on other types of distillates cannot be interpreted without a certain degree of ambiguity. The concentration field of total sulphur content sulphur corresponds to a concentration field of sulphured molecules (BTs + DBTs) of approximately 1-12% m/m.

The results plotted on Figure 3a show that the global contents (BTs + DBTs) are overestimated by approximately 30% by MS. The deviations noted for BTs are rather significant and may even reach 60% in some cases (Fig. 3b). The DBTs are underestimated by 20% in average (Fig. 3c). If we admit that purely technical parameters, linked with the implementation of the apparatus, are controlled and the scope of the method is adhered to, the errors associated with MS should be sought after in the calibration of quantitative calculation, i.e. in the coefficients linking the concentrations of the groups to the measured intensities. The calculation of the concentrations of each group-type by MS is governed by the following formula:

$$C = S^{-1} \cdot \Sigma$$

where C is the concentration matrix, Σ that of the sums of the intensities of the characteristic ions and S is a matrix regrouping the average response coefficients of each group (diagonal of the matrix) as well as cross-referenced terms that take into account intergroup contributions. The accuracy of the analysis therefore depends on two things: accuracy of the average response coefficients and correct evaluation of all interference phenomena of one group on the others. Both these items have been checked.

3.2 Accuracy of the Response Coefficients

In order to check the average response coefficients ascribed to both groups of sulphured aromatic compounds in the MS method [5], a mixture of model molecules, as a solution in toluene, was produced. It consists non-alkylated molecule (benzothiophene and dibenzothiophene) as well as certain alkylated forms up to three carbons for the BTs and two carbons for the DBTs. The detailed list of the molecules used is given in Table 1.
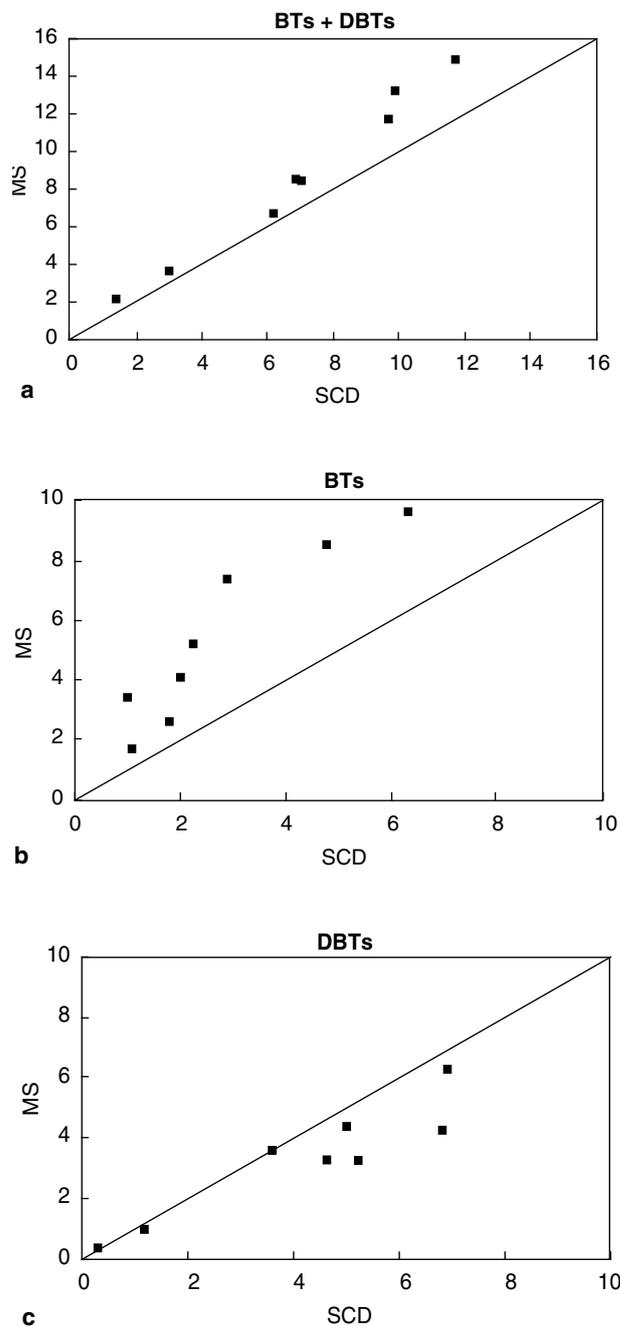

a

b

c

Figure 3

Comparison of BTs and DBTs quantification (%m/m) by MS and GC/SCD.

This mixture was analysed in three ways:

– by GC/FID (flame ionising detector);
– by direct MS;
– by GC/MS, while integrating the surface of the peaks of the fragmentogram resulting from the sum of the characteristic ions used for quantification of the sulphured molecules.

TABLE 1

Reference mixture of BTs and DBTs

Group-type	BT	DBT
Isomers present	BT	DBT
	M3-BT	M1-DBT
	M4-BT	M2-DBT
	M6-BT	M3-DBT
	M7-BT	M4-DBT
	DM2,3-BT	DM1,3-DBT
	DM2,5-BT	DM1,2-DBT
	TM2,3,4-BT	DM1,4-DBT
	TM2,3,6-BT	DM2,3-DBT
	TM2,5,7-BT	DM2,8-DBT
		DM4,6-DBT

The GC/FID analysis was considered as the reference analysis for this mixture, which does not raise any separation or specific detection problems. On the basis of the GC/MS analysis, the characteristic fragmentograms of the BTs and DBTs have been reconstructed on computer (Fig. 4a and b). This means that, for each spectrum acquired during elution of the compounds of the mixture, both following sums were calculated:

– sum of the intensities of the ions $133.01 + n * 14.0156$ ($n = 0$ to 7) + sum of the intensities of the ions $134.02 + n * 14.0156$ ($n = 0$ to 7) to follow the BTs;

– sum of the intensities of the ions $183.03 + n * 14.0156$ ($n = 0$ to 4) + sum of the ions $184.03 + n * 14.0156$ ($n = 0$ to 4) to follow the DBTs.

Plotting the values of these sums in relation to time, hence to chromatographic elution can produce two fragmentograms: these are the selective traces of the BTs and of the DBTs. The surface of each peak has been integrated and the BTs and DBTs content calculated while using the response coefficients of the method [5].
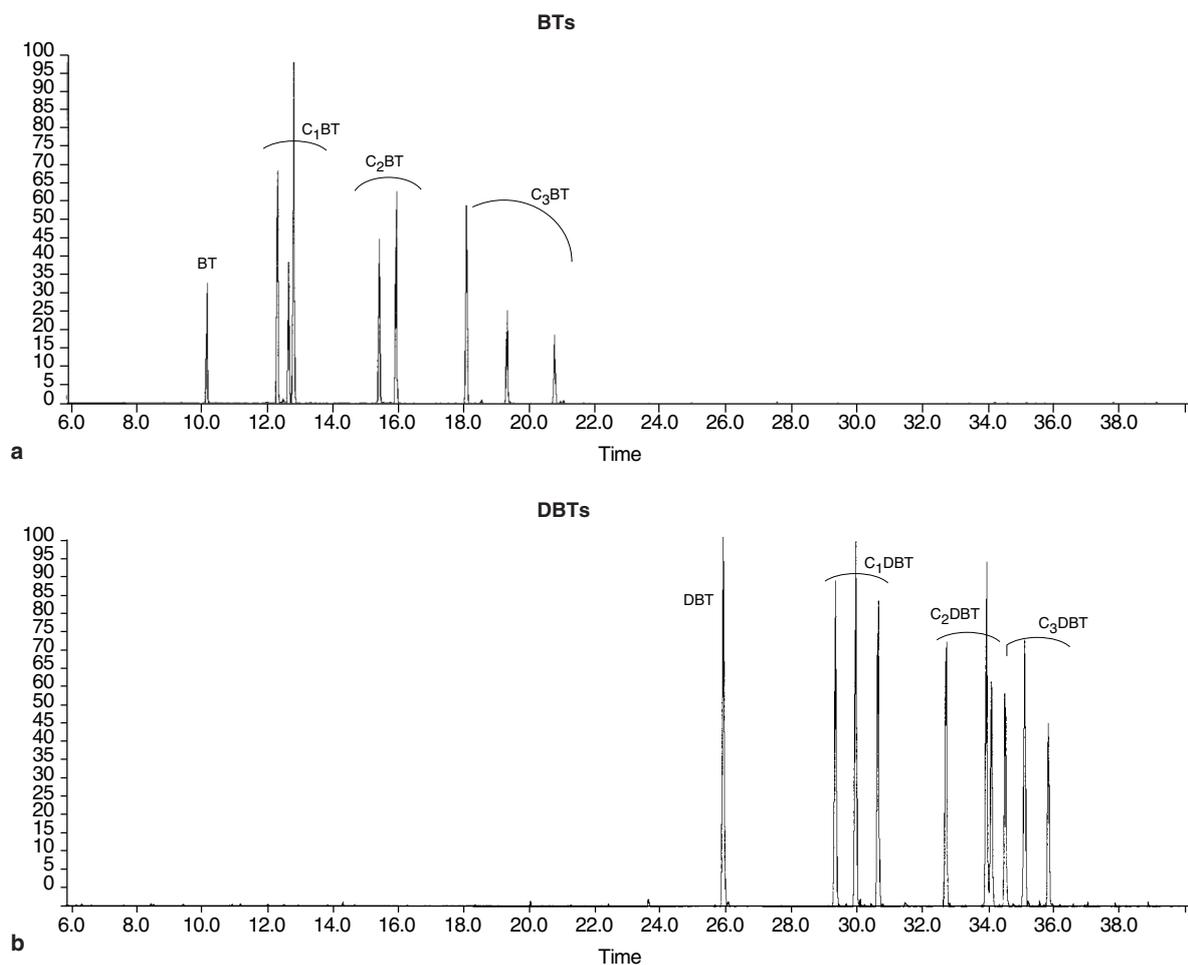

Figure 4

GC/MS fragmentogram of a test mixture: a: BTs ; b: DBTs.

Comparison of the results obtained by the three methods is reported in Table 2. Good matching of results can be obtained, within the repeatability limit of the methods. It is therefore possible to conclude that the average response coefficients used are corrects and should not be held responsible for the significant deviations observed between MS and SCD.

TABLE 2

Comparison of the %m/m dosage of the BTs and DBTs of the reference mixture

%m/m	SC/FID	GC/MS	MS
BTs	57 ± 2	60 ± 4	59 ± 3
DBTs	43 ± 2	40 ± 3	41± 2

3.3 Accuracy of Intergroup Contributions

The second possible cause of error being poor evaluation of interference between groups, a more detailed study, at middle resolution GC/MS ($R = 5000$) was undertaken. The samples studied are a LCO (GO 2) and a HCO (GO 6) hat exhibit significant deviations when dosing BTs and DBTs.

The first step consisted in reconstructing the fragmentograms of the specific ions of the sulphured compounds, as explained in the previous paragraph.

The sulphured molecules present in these samples being exclusively in the form of thiophenic aromatics, it is possible to compare directly the BTs and DBTs fragmentograms with the SCD chromatogram, knowing that the latter is equivalent to the sum of both MS traces (Figs. 5 and 6).

This survey puts in evidence, in the MS trace of the BTs, the presence of additional peaks (located on Fig. 5b by *). If we study the GO 6, these spurious peaks are even more significant and even constitute the predominant peaks in the fragmentogram (Fig. 6b).

Thanks to the spectra acquired throughout the chromatogram, it has been possible to identify the interfering molecules. These are triaromatic compounds, such as phenanthrene and anthracene as well as their alkylated derivates $M = 178.078 + n*14.016$). While studying these spectra, for example that of methyl-phenanthrene ($M = 192$), we can observe that the latter exhibits ions with masses 189 and 190 which correspond to the departure of two and three hydrogen atoms (M-2 and M-3) during the fragmentation in the source (Fig. 7). These triaromatic compounds have a raw formulas C_nH_{2n-18}. The fragments have therefore the following raw formulas: C_nH_{2n-20} and C_nH_{2n-21}. In the resolution conditions used ($R = 5000$), these fragments interfere with the ions of formulas C_nH_{2n-10} S and C_nH_{2n-11} S which are the characteristic ions of the benzothiophenes. These ions are thus counted in the characteristic sum of the BTs. While examining the group interaction matrix [5], it seems that the contribution term of the C_nH_{2n-18} on the C_nH_{2n-10} S is nil. This interaction

has therefore not been taken into account and explains the bad quantification of the BTs. It is the more significant in the GO 6 as it contains a high quantity of C_nH_{2n-18} (12.5% m/m).

3.4 Determination of the Interaction Terms

In order to correct the method, it has been necessary to determine the value of the cross-referenced term due to interference caused by the triaromatic compounds (C_nH_{2n-18}) on the BTs (C_nH_{2n-10} S). This term has an average value since it must take into account all the representatives of the triaromatic group. We must therefore consider the non-alkylated molecule (phenanthrene or anthracene) but also the alkylated forms and their isomers and study their mass spectrum in order to determine, in each case, their contribution to the sum of the characteristic ions of the C_nH_{2n-10} S. Thanks to GC/MS coupling on the GO 6, it is possible to isolate the spectra of the phenanthrene, C_1, C_2 and C_3-phenanthrenes and to calculate the resulting MS analysis. The anthracene spectrum being similar to that of the phenanthrene, we have postulated that it contributes in the same way to the sum of the characteristic ions of the BTs. The results are reported in Table 3 and show that regardless of the length of the alkyle chain and whatever its isomerism, the ion contribution by the triaromatic compounds to the sum of the characteristic ions of the BTs is similar and close to 25-26% of the sum of the characteristic ions of the C_nH_{2n-18}. Only the non-alkylated molecule generates a smaller value (18%). The average contribution has been therefore assessed at 25% and integrated to the calculation matrix.

TABLE 3

Contribution of $C_n H_{2n-18}$ ions to the characteristic sum of the BTs

Compound	Contribution to BT (%)
Phenanthrene/Anthracene	18
C_1-Phenanthrene/Anthracene	26
C_2-Phenanthrene/Anthracene	25
C_3-Phenanthrene/Anthracene	26

3.5 Correction of the Sulphured/Polyaromatic Compound Interference

When samples exhibit a high content in molecules distilling above 350°C, overlapping phenomena can be observed between polyaromatic and sulphured compounds as explained at paragraph 1.1. These interferences can be corrected by calculating the total ratio of sulphured molecules as determined on the basis of the total sulphur content, the average molecular mass of the sulphured molecules of the sample and its comparison with the contents obtained by MS. The following formula is used:

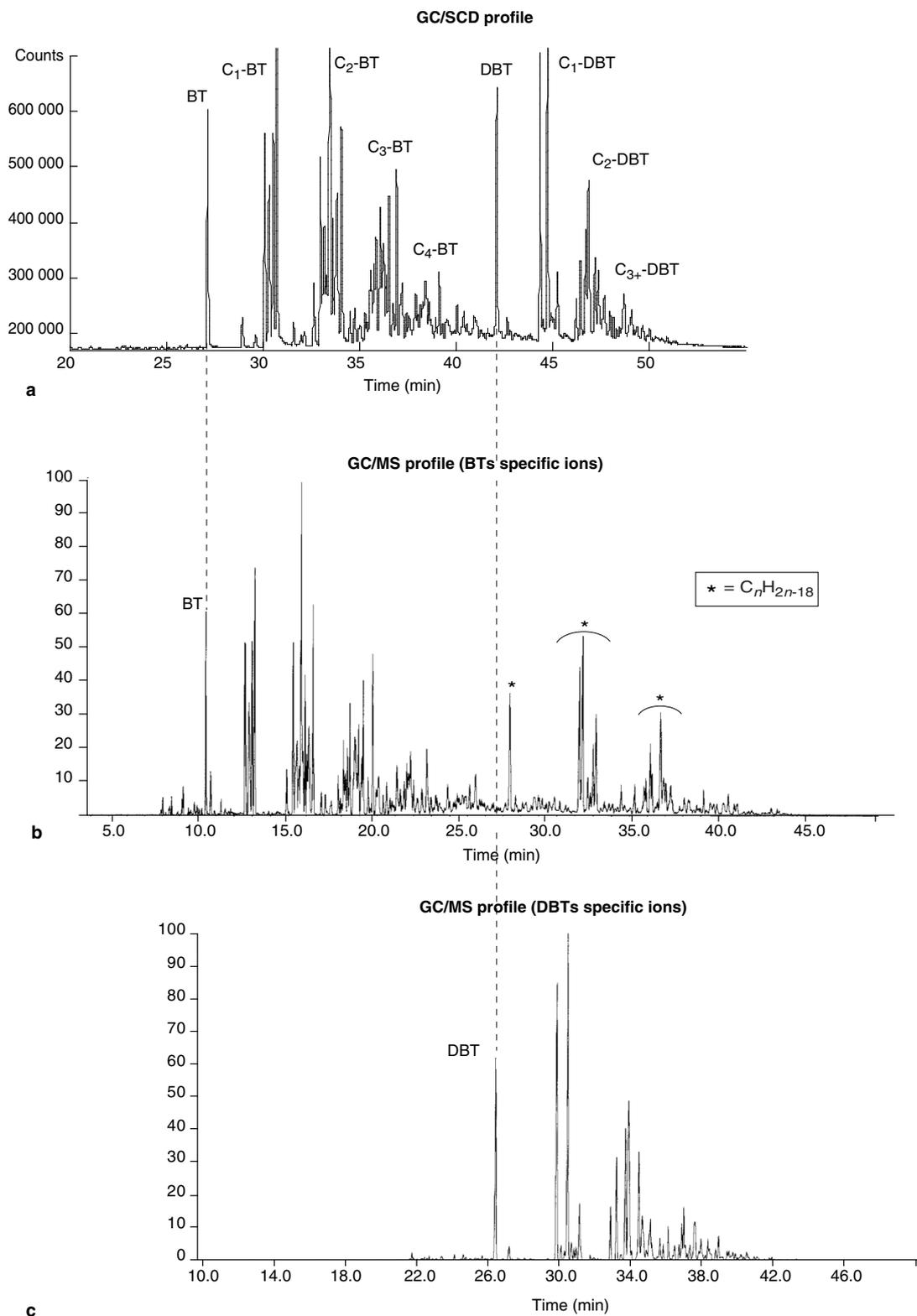$$(\% \text{ m/m sulphured molecules}) = \%S * M/32$$

GC/SCD profile

a

GC/MS profile (BTs specific ions)

$\star = C_nH_{2n-18}$

b

GC/MS profile (DBTs specific ions)

c

Figure 5

Comparison of BTs and DBTs specific profile in MS and GC/SCD of an LCO (GO 2).

GC/SCD profile

GC/MS profile (BTs specific ions)

$\star$ = C_nH_{2n-18}

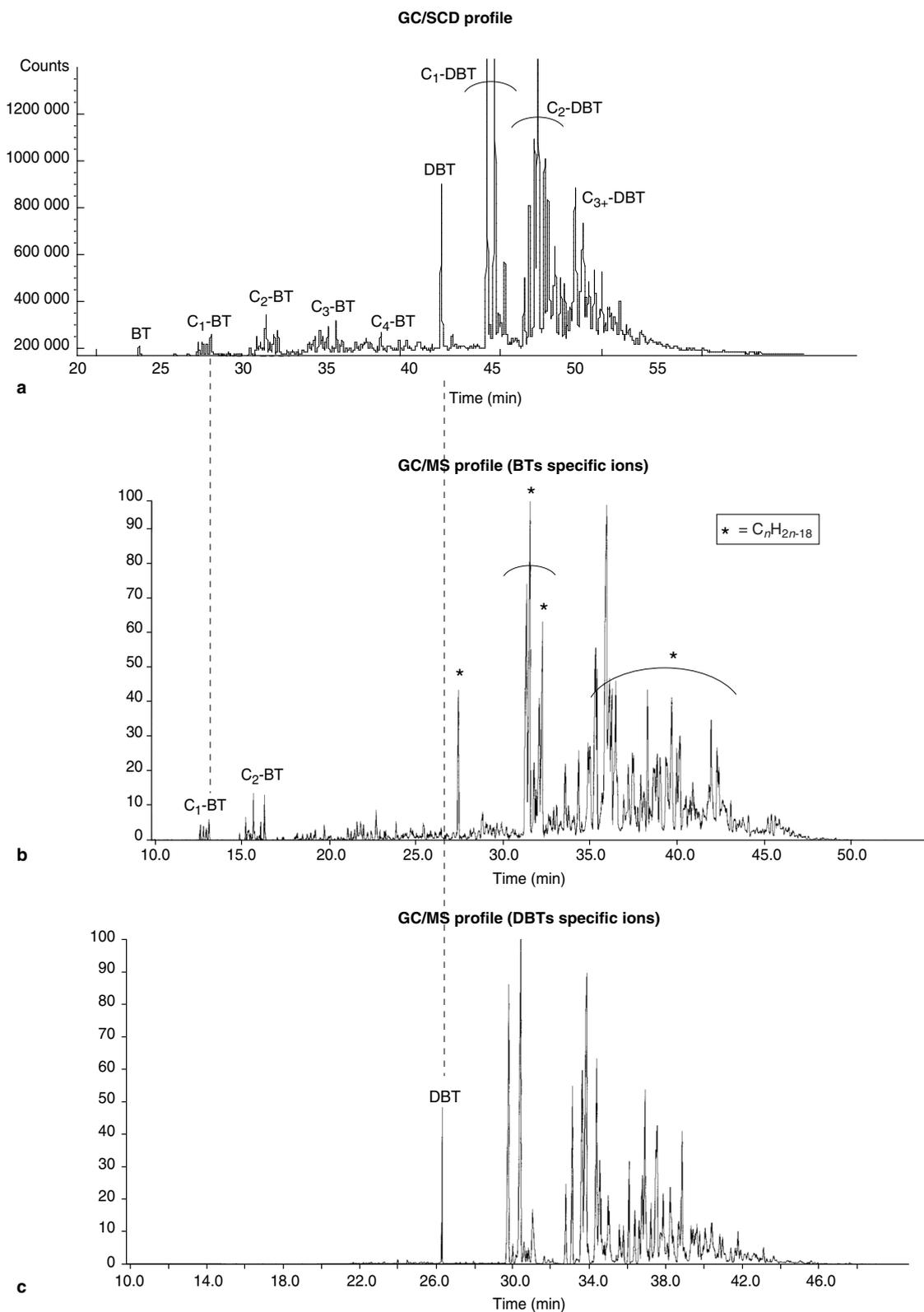**GC/MS profile (DBTs specific ions)**

Figure 6

Comparison of BTs and DBTs specific profile in MS and GC/SCD of an HCO (GO 6).

with:

%S % m/m total sulphur content of the whole sample (determined by X fluorescence or combustion);

M average molecular mass of the sulphured molecules of the sample.

The average molecular mass of the sulphured compounds M is calculated on the basis of the average mass spectrum of the sample from which is derived the distribution of the molecular ions of each group-type of sulphured compounds. These peaks are significant of the non-fragmented molecules. Figure 8 shows an example of distribution of the molecular peaks of benzothiophenes in a middle distillate. The BTs distribution is obtained after correction of each intensity of both contributions:

– the contribution due to fragmentation of the triaromatic compounds and assessed as 25% of the intensity of the corresponding fragment;

– the contribution due to isotopic contribution of the ^{13}C of the ions of mass M-1 and equal to 1.1% of the number of carbon atoms of the interfering ion.

For example, the intensity of the ion 176, which corresponds to the C_3-BTs, will be corrected by 25% of the intensity of the 178 (peak of the phenanthrene) and by 12.1% of the intensity of the ion 175 which comprises eleven carbon atoms. The DBTs ions will only be corrected by the isotopic contribution.

By postulating, at first approximation, that all the response coefficient of each individual in the group-type are similar, it is possible to calculate the average molecular mass of the group considered. The average molecular mass of the sulphured molecules of the sample is obtained by carrying out the same operation on both groups of sulphured compounds and by weighing each mass by the corresponding concentration.

The positive difference between the % m/m of sulphured molecules determined by mass spectrometry and that calculated on the basis of the data from the elemental analysis is then ascribed to the polyaromatic compounds. It should be noted that for non-LCO distillates, the values derived from the elementary analysis can be greater than those of the MS because of the presence, in certain samples, of non-thiophenic sulphured molecules such as sulfides. In such a case, this correction cannot be applied. Any interference should then be minimised while limiting the ratio of samples distilling above 350°C.

4   VALIDATION OF THE CORRECTION

After checking the average response coefficients of the group-types of sulphured compound for accuracy, the corrections made to quantitative calculation of the MS method described at [5] can be summed up threefold as follows:

– taking into account the contribution of the triaromatic group-type when calculating the BTs;

– assessing the average molecular masses of the BTs and DBTs group-types on the basis of the distributions of the interference-corrected molecular peaks;

– taking this data into consideration when correcting interference between sulphured and polyaromatic compounds by comparison with elemental analysis of sulphur.

The corrected MS method was applied to the eight middle distillates and the results obtained were compared to those of GC/SCD.

The first step consisted in validating the calculation of the average molecular mass of the thiophenic sulphured compounds. These masses, estimated by MS and by
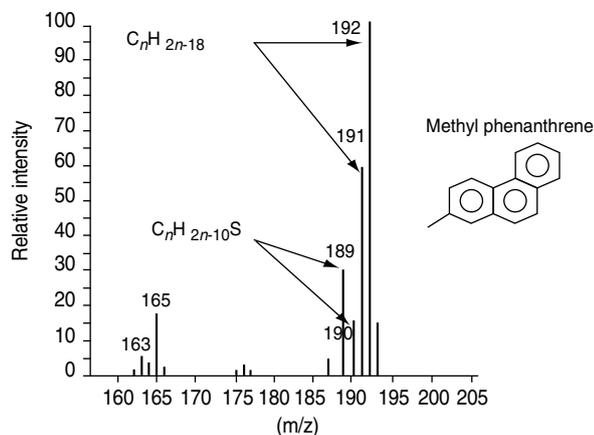
Figure 7

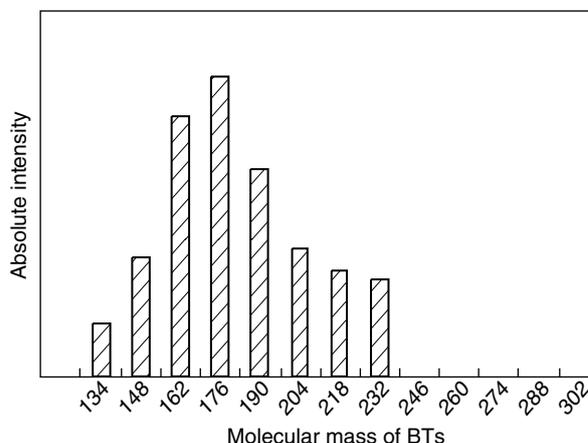Mass spectrum of the methyl phenanthrene.

Figure 8

Distribution of the BT molecular peaks in an average distillate.

GC/SCD are reported at Table 5. Both techniques match rather well and this validates the fact that the same response coefficient was ascribed to all BTs and DBTs molecules, whatever the length of their alkyle chains. However, 10-15% deviations from the mass value can be noted for the BTs when the 350^+ ratio of the middle distillate exceeds 20% m/m.

TABLE 4

Characteristics of the LCO used for MS/SCD comparison

	%S (%m/m)	T_{50} (°C)	$\%C_nH_{2n-18}$ (%m/m)	$\%350^+$ (%m/m)
GO 1	0.26	261	1.6	0
GO 2	0.50	261	2.2	5
GO 3	1.13	290	5.2	10
GO 4	1.76	281	5.7	15
GO 5	1.13	303	9.1	20
GO 6	0.90	348	12.5	30
GO 7	1.97	321	6.7	40
GO 8	1.56	336	7.4	40

TABLE 5

Comparison of average molecular masses obtained by MS and GD/SCD

M	$\%350^+$ (%m/m)	BT		DBT	
		SCD	MS	SCD	MS
GO 1	0	166	165	199	198
GO 2	5	166	164	202	202
GO 3	10	170	172	211	209
GO 4	15	165	167	207	202
GO 5	20	172	178	212	215
GO 6	30	171	196	209	212
GO 7	40	165	186	211	214
GO 8	40	173	187	215	217

TABLE 6

Comparison of the %BTs and %DBTs obtained by corrected MS and GC/SCD

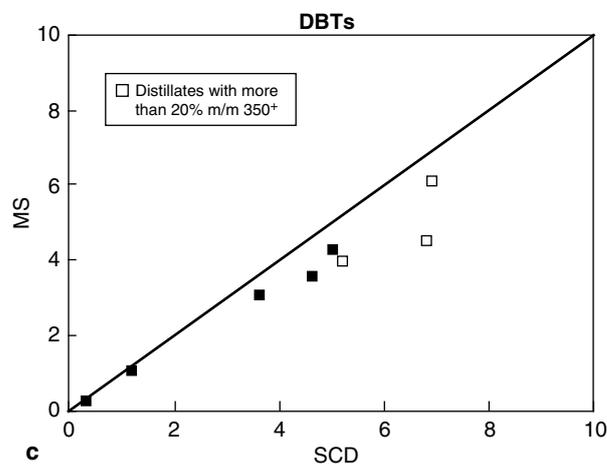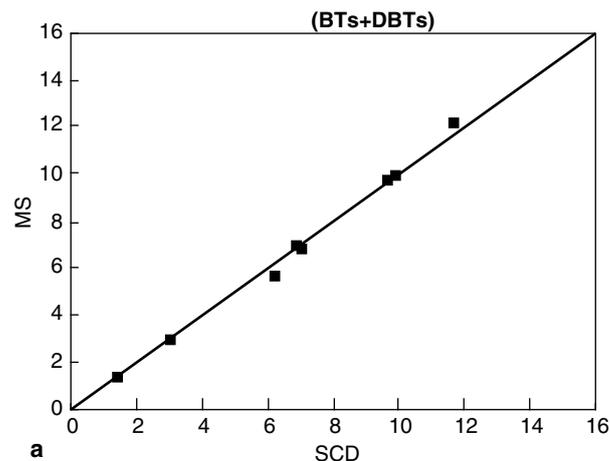| M	$\%350^+$ (%m/m)	BT (%m/m)		DBT (%m/m)	
		SCD	MS	SCD	MS
GO 1	0	1.1	1.1	0.3	0.3
GO 2	5	1.8	1.8	1.2	1.1
GO 3	10	2.0	2.6	5.0	4.3
GO 4	15	6.3	6.8	3.6	3.1
GO 5	20	2.3	3.3	4.6	3.6
GO 6	30	1.0	1.7	5.2	4.0
GO 7	40	4.8	6.1	6.9	6.1

| GO 8 | 40 | 2.9 | 5.2 | 6.8 | 4.5 |

Figure 9

Comparison of BTs and DBTs quantification (%mm) by corrected MS and GC/SCD (to be compared with Figure 3

GC/SCD profile

Counts

a

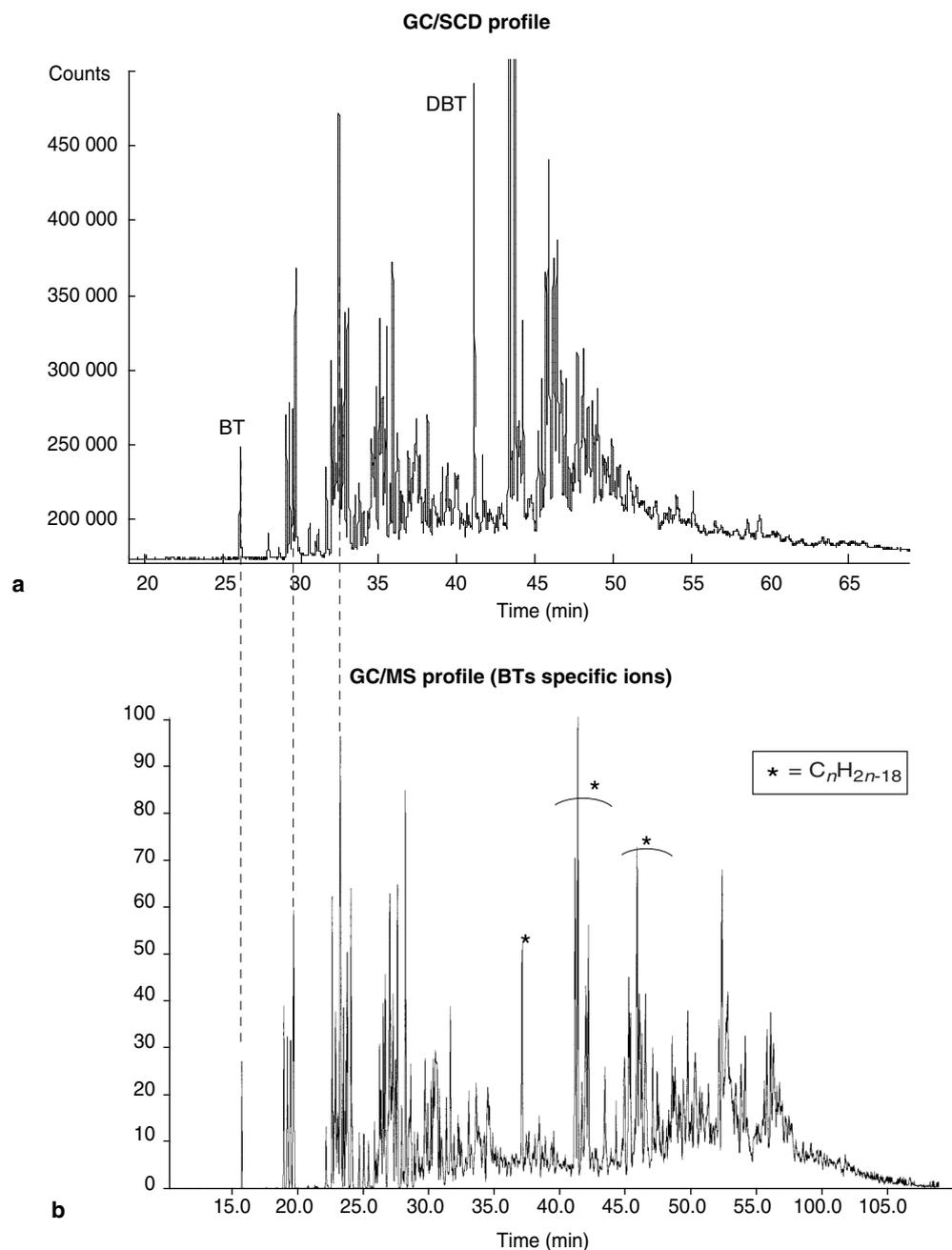**GC/MS profile (BTs specific ions)**

$\star = C_nH_{2n-18}$

b

Figure 10

Comparison of BTS specific profile in MS and GC/SCD of a heavy LCO (GO 8)

The BTs and DBTs concentrations, obtained by the corrected method, are specified at Table 6. Comparing Figure 9 and Figure 3 enables to appreciate the improvement of the results with respect to the MS method before correction as well as the deviations still provided with GC/SCD.

As regards the total concentration (BTs + DBTs), both techniques match very well (Fig. 9a). This improvement is essentially due to better assessment of molecular masses in MS. Indeed, both techniques are based on the total sulphur

content: for polyaromatic correction in MS (§ 3.5) and for calculating the % of sulphured molecules from peaks area in GC/SCD (§1.2).

As regards the distribution among BTs ands DBTs group-types, significant improvement on the BTs can be observed, which confirms the weight and the relevancy of the corrections made, which corrections relate mainly to this group-type. Nevertheless, deviations subsist, the BTs remaining overestimated (Fig. 9b) and the DBTs (Fig. 9c) underestimated in relation to the GC/SCD results. It should

be noted that the residual deviations are not linked to the sulphur content. Indeed, the GO 4, which exhibits one of the highest contents (1.76% m/m) can be found on the parity line. The largest deviations are shown by the heaviest distillates or by those whose final boiling point is high, hence high 350^+ content: GO 6, GO 7, GO 8 (Table 4). The latter elements are represented on Figures 9b and 9c by the symbol □. While limiting comparison to the samples whose distilled fraction above 350°C is smaller than 20% m/m, good correlation of the results can be obtained between MS and GC/SCD, whereby the average deviation on the group-types is approximately 10% rel.

In fact, comparing the results on the heaviest distillates is impeded by the limits of the scope of both techniques. In MS, on the one hand, the heaviest fraction may be vaporised poorly in the inlet system of the spectrometer. On the other hand, it probably contains polyaromatic compounds which have not been taken into account and which are liable to affect the estimate of the sulphured compounds. In GC/SCD, the presence of a high 350^+ content raises issues of chromatographic separation which may compromise integration of the peaks ascribed to BTs and BTs group-types.

Indeed, the BTs are dosed while integrating all the peaks eluted between the beginning of the benzothiophene and the beginning of the DBT. Over this range, the alkylbenzothiophenes, the length of whose alkyle chains contains zero to four atoms of carbon, are eluted. This means that the benzothiophenic derivates whose aliphatic chains contain more than four atoms of carbon are eluted after the DBT. The higher the final boiling point, the greater the probability to obtain heavy alkylBTs. The SCD chromatogram shows a non-resolved signal under the DBT and its first alkylated forms for certain samples as in the case of the GO 8 (Fig. 10a). These upper derivates are then counted as DBTs and not as BTs any longer. The GC/SCD would therefore tend to overestimate the DBTs and to underestimate the BTs, which is borne out by our observations. This is confirmed by the MS fragmentogram of the characteristic ions of the BTs. These ions are plotted on Figure 10. At elution times greater than that of the DBT, apart from the peaks caused by the triaromatic compounds (identified by an *, a non resolved signal can be seen, which is surely due to the response of the alklyBTs to a certain extent, whose number of isomers is very large and which do not generate thin peaks any longer, but a broad signal. These cuts may also comprise naphthalenothiophenes which are eluted in this zone and which, therefore, would be detected by GC/SCD, thus contributing to the overestimate of the DBTs.

The discrepancy observed between both methods, for heavy distillates, is therefore ascribable to MS as well as to GC/SCD and is consistent with the restrictions shown by both techniques.

CONCLUSION

Using intertechnique comparisons (MS-GC/SCD), a bias could be put in evidence in the quantification of sulphured molecules by the method MS described previously [5]. Interference of triaromatic on benzothiophenic compounds, not taken into account until now, could be detected and this influence could be corrected. This modification has been validated on middle distillates derived from catalytic cracking, since these are the sole distillates for which quantitative determination of the BTs and of the DBTs can be performed by GC/SCD without any bias. By considering exclusively the samples falling perfectly into the scope of both methods (350^+% < 20%m/m), the approach used to improve the quantification of sulphured compounds could be reinforced without any reservation.

The corrected method applies to the other types of middle distillates, derived from direct distillation or other conversion processes since interferences remain the same, because the presence of other types of sulphured molecules (other than BTs and DBTs) does not cause any additional disturbance.

Moreover, for samples whose 350^+ content is nil, the difference between the ratio of sulphured molecules as determined by MS and that calculated from the elementary analysis gives access directly to the content of another type of sulphured compounds.

We therefore have now a method whose accuracy has been improved and which provides in a single and quick analysis (15 min), detailed distribution of the group-types and the value of the average molecular masses of the thiophenic sulphured aromatic group-types.

ACKNOWLEDGMENTS

REFERENCES

1 Durand, J.P., Béboulène, J.J. and Ducrozet, A. (1995) *Analusis*, **23**, 481-483.

2 Snyder, L.R., Howard, H.E. and Ferguson, W.C. (1963) *Anal. Chem.*, **35**, 11, 1676.

3 *ASTM D2425 Annual Book of ASTM Standards*, **24**, 367-374, (1980).

4 Bouquet, M. and Brument J. (1990) *Fuel Science and Technology INTL*, **8,** 9, 961-986.

5 Castex, H., Boulet, R., Juguin, J. and Lepinasse, A. (1983) *Rev. Inst. franç. du pétr.*, Editions Technip, **38**, 4, 523-532.

6 Robinson, C.J. and Cook, G.L. (1969) *Anal. Chem.*, **37**, 792.

7 Fisher, I.P. and Fischer P. (1974) *Talanta*, **21**, 867-875.

8 Lumpkin, H.E. and Aczel, T. (1976) High Performance Mass Spectrometry. *ACS Symposium* series 70, Washington, 261-273.

9 *ASTM D2549-91 Annual Book of ASTM Standards* (1991).

10 *CEN/TC19/WG18 Meeting*, European Commitee for Standardization, Bruxelles, 4 june 1993.

11 Cookson, D.J., Rix, C.J., Shaw, I.M. and Smith, B.E. (1984) *J. Chromatography*, **312**, 237.

12 Burdett, R.A., Taylor, L.W. and Jones, L.C. (1954) Molecular Spectroscopy. *Rept. Conf, Ins, Petroleum*, 30-41, London.

13 *ASTM D5186-91 Annual Book of ASTM Standards* (1991).

14 Qian, K., Hsu, C.S. (1992) *Anal. Chem.*, **64**, 2227-2232.

15 Dzidic, I., Petrerson, H., Wadsworth, P. and Hart, H. (1992) *Anal. Chem.*, **64**, 2227-2235.

16 Fafet, A., Magne-Drisch, J. (1995) *Rev. Inst. franç. du pétr.*, **50**, 3, 391-404.

17 Baco, F., Bré, A. and Quignard, A. (1993) *15th International Symposium of Capillary Chromatography*, Riva del Garda, **2**, 1385-1395, Ed. Huethig.

18 Depauw, G.A. and Froment, G.F. (1997) *Journal of chromatography A*, **761**, 231-246.

19 Lopez-Garcia, C., Paisse, O., Bré, A., Grenier-Loustalot, M.F. and Szymanski, R. (1998) *15th Internatioal Mass Spectrometry Conference*, Lyon, 23.