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

Second Part: Development and Validation of a New Inlet System for Heavy Cuts

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This paper constitutes the second part of a paper devoted to improvements of mass spectrometry methods for group-type analysis of petroleum cuts. In the first part (*Rev. IFP*, Vol. 54, (1999), No. 4, pp. 439-452), the accuracy of the quantification of sulphured aromatic compounds in middle distillates was evaluated using intertechnique comparisons. Interference of triaromatic on benzothiophene compounds, not taken into account until now, could be detected and a correction procedure was proposed.

INTRODUCTION

No analytical technique enables us to gain perfect knowledge of the molecular composition of high molecular weight petroleum cuts (mass ranging from 300 to 1000 u.m.a.). The technique used most frequently to characterise these samples consists in separating them by liquid chromatography [1] into 3 large chemical group-types (aliphatic hydrocarbons, aromatic hydrocarbons, resins), since the asphaltenes have been eliminated and dose previously by precipitation. Until now, only electronic bombardment and high resolution mass spectrometry, thanks to group-type analysis methods, gives access to the detail of the various chemical group-types. More especially, one of them [2, 3] enables quantifying 33 chemical group-types, without any previous separation.

The first step of this analysis consists in vaporising the sample into the source of the mass spectrometer. Still, these cuts are made up of molecules whose boiling point lies above 350°C (at atmospheric pressure) which corresponds to the beginning of thermal cracking of organic molecules and their final boiling point is often higher than 600°C.

This point is a crucial element and the mass spectrometer must therefore be fitted with a powerful inlet system. However, very few of them exhibit the required characteristics. Recently, the use of new inlet modes such as field ionisation or field desorption (FI/FD) have enabled to break free from this vaporisation step and molecular mass profiles could be obtained. But not a single reliable quantitative data on detailed composition could be extracted, failing any response coefficient or resolution [4, 5]. Moreover, optimising the adjustments of spectrometer source can prove rather tricky. Finally, these protocols often call for long prior separations.

A new system has therefore been developed, then tested in order to improve conventional electronic bombardment analyses at 70 eV. It combines the advantages of both systems currently available on the market, while limiting their shortcomings.

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 bien 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 (*Rev. IFP*, Vol. 54, (1999), N° 4, 439-452), la justesse de la quantification par SM des composés soufrés thiophéniques dans les distillats moyens est étudiée par comparaison intertechnique 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.

Dans cette seconde partie, un nouveau système d'introduction de l'échantillon dans la source du spectromètre, dédié à l'analyse par famille des coupes lourdes est décrit. Sa validation, par comparaison des résultats de SM avec ceux de la chromatographie liquide (CL), ainsi que ses performances, sont exposées.

Mots-clés : spectrométrie de masse, analyse quantitative par famille, résidus et distillats sous vide, système d'introduction, chromatographie liquide.

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 (*Rev. IFP*, Vol. 54, (1999), No. 4, pp. 439-452), 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 this 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, vacuum distillates and residues, inlet system, liquid chromatography.

1 DESCRIPTION OF THE GROUP-TYPE ANALYTICAL METHOD

The method used is an adaptation of that described by Bouquet *et al.* [3]. Its scope covers the petroleum cuts whose boiling point ranges from 240 to 700°C. It does not call for, theoretically, prior separation, unlike other methods [6-9].

It is conducted with 70 eV electronic impact and high resolution (10 000) in order to separate the groups having the same nominale mass. It quantifies 31 group-types (in %m/m) among which 3 aliphatic (paraffins, non-condensed naphthenes and condensed naphthenes with 2, 3 and 4 rings), 13 aromatic (with one to five condensed rings) and 15 sulphured and disulphured aromatic compounds. The detail of these group-types is given at Figure 1, as well as a non-exhaustive list of developed formulae liable to correspond to each raw formula. The contribution of each group-type is determined by the sum of the M^+ molecular peaks and/or fragment peaks $(M-H)^+$.

Conversely, it only quantifies pure hydrocarbons or sulphured aromatic compounds. This means that resins and *a fortiori* asphaltenes are not taken into account. This constitutes the first restriction of the method and we shall endeavour at a later stage to specify their influence on the results.

The second restriction relates, as for the middle distillates, to the interferences between chemical group-types. This method is conducted with high resolution (10 000). It is indeed necessary to separate ions of identical nominale mass but of different exact mass. Figure 2 represents a portion of the mass spectrum of a heavy cut. We can see, at the nominale mass 295, a multiplet constituted of 4 clearly resolved peaks, each at a distance of approximately 0.1 u.m.a. from its neighbour. They correspond to 4 chemical interfering group-types, which are:

- paraffins (C_nH_{2n+2});
- alkylnaphthalenes (C_nH_{2n-12});

Group-type	Formula				
C_nH_{2n+2}					
C_nH_{2n}					
C_nH_{2n-2}					
C_nH_{2n-4}					
C_nH_{2n-6} (naphthenes)					
C_nH_{2n-6} (aromatic compounds)					
C_nH_{2n-8}					
C_nH_{2n-10}					
C_nH_{2n-12}					
C_nH_{2n-14}					
C_nH_{2n-16}					
C_nH_{2n-18}					
C_nH_{2n-20}					
C_nH_{2n-22}					
C_nH_{2n-24}					
C_nH_{2n-26}					
C_nH_{2n-28}					
C_nH_{2n-30}					

C_nH_{2n-10S}	
C_nH_{2n-12S}	
C_nH_{2n-14S}	
C_nH_{2n-16S}	
C_nH_{2n-18S}	
C_nH_{2n-20S}	
C_nH_{2n-22S}	
C_nH_{2n-24S}	
C_nH_{2n-26S}	
C_nH_{2n-28S}	
$C_nH_{2n-20S_2}$	
$C_nH_{2n-22S_2}$	
$C_nH_{2n-24S_2}$	
$C_nH_{2n-26S_2}$	
$C_nH_{2n-28S_2}$	
$C_nH_{2n-30S_2}$	
$C_nH_{2n-32S_2}$	

Figure 1

Description of the quantified molecules.

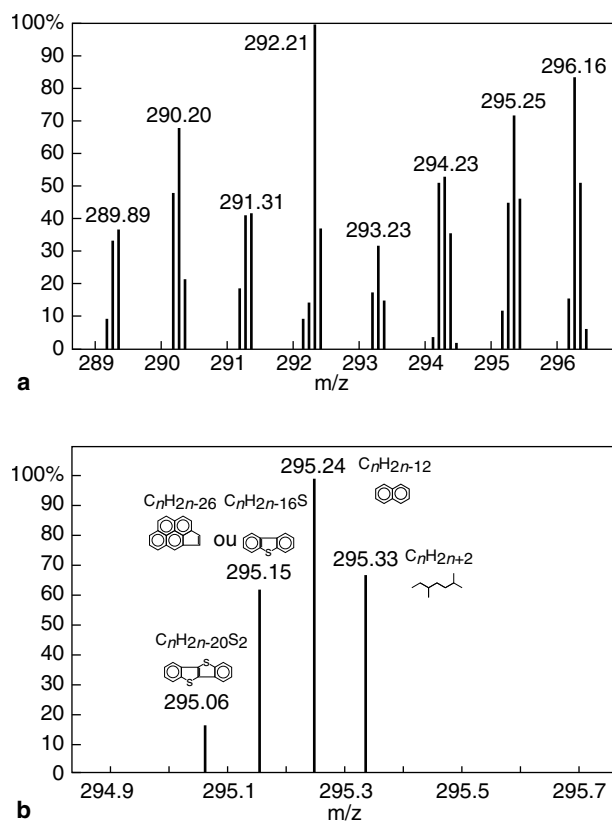


Figure 2

Details of the mass spectrum of a heavy cut.

a: mass range 289-297 a.m.u.;

b: mass range 294.9-295.7 a.m.u.

- alkyltetraaromatic or alkyldibenzothiophenes (C_nH_{2n-26} or $C_nH_{2n-16}S$);
- alkyldisulphured compounds ($C_nH_{2n-20}S_2$).

This kind of interference appears for each mass rating since numerous chemical group-types are present in these mixtures. These interferences are summed up in Table 1.

However, even at this resolution, certain interferences have not been eliminated. They relate to the sulphured aromatic compounds and to the polyaromatic compounds and can only be removed when working at 80 000 resolution, which is impossible to achieve while maintaining correct sensitivity. The method still endeavours to quantify them, based upon the hypothesis that, in a distillation cut, the sulphured aromatic compounds are more polar than pure aromatic compounds. Their molecular mass is therefore smaller, in average. Consequently, in the series of the ions characterising both these group-types, the following approximation is made: the low mass ions will be considered as belonging mainly to the sulphured compounds and the high mass ions as belonging to the pure aromatic compounds.

TABLE 1

Interferences between group-types

C_nH_{2n+2}	C_nH_{2n-12}	C_nH_{2n-26} $C_nH_{2n-16}S^*$	$C_nH_{2n-20}S_2$
C_nH_{2n}	C_nH_{2n-14}	C_nH_{2n-28} $C_nH_{2n-18}S^*$	$C_nH_{2n-22}S_2$
C_nH_{2n-2}	C_nH_{2n-16}	C_nH_{2n-30} $C_nH_{2n-20}S^*$	$C_nH_{2n-24}S_2$
C_nH_{2n-4}	C_nH_{2n-18}	C_nH_{2n-32} $C_nH_{2n-22}S^*$	$C_nH_{2n-26}S_2$
C_nH_{2n-6}	C_nH_{2n-20} $C_nH_{2n-10}S^*$	C_nH_{2n-34} $C_nH_{2n-24}S^*$	$C_nH_{2n-28}S_2$
C_nH_{2n-8}	C_nH_{2n-22} $C_nH_{2n-12}S^*$	C_nH_{2n-36} $C_nH_{2n-26}S^*$	$C_nH_{2n-30}S_2$
C_nH_{2n-10}	C_nH_{2n-24} $C_nH_{2n-14}S^*$	C_nH_{2n-38} $C_nH_{2n-28}S^*$	$C_nH_{2n-32}S_2$

* interferences non removed at R: 10 000.

Thus, the alkyldibenzothiophenes will be quantified by the ions of mass 147.02 to 217.10 and the alkyldihydropyrenes (triaromatic of formula C_nH_{2n-20}) by the ions 231.11 to 623.55. The method, after calibration on samples derived from direct distillation, will give accurate results for samples of the same origin. Conversely, for cuts derived from other processes, it is necessary to control this accuracy by calculating the percentage of sulphured molecules contained in the sample on the basis of its elemental sulphur content ratio and of its molecular mass (see first part). Comparison with the content provided by mass spectrometry is carried out. If this value is greater than the value calculated from the elemental analysis, the difference is allocated to the polyaromatic compounds.

2 IMPROVING THE INLET SYSTEM FOR HEAVY CUTS

2.1 Commercially Available Systems

As we have said previously, the sample must be vaporized before introduction into the source of the spectrometer, which is, under secondary vacuum. There are two types of inlet system on the market, the batch inlet system and the solid probe.

The first system (Fig. 3a) consists of a heated reservoir, approximately 0.5 l, and placed under primary vacuum. The sample is introduced thanks to a crucible, which communicates with the reservoir via a primary vacuum lock. Vaporisation usually takes place by additional heating around the crucible or by thermal diffusion from the reservoir to the crucible. Molecular leak enables transferring an aliquot fraction of the sample towards the ion source. The advantage

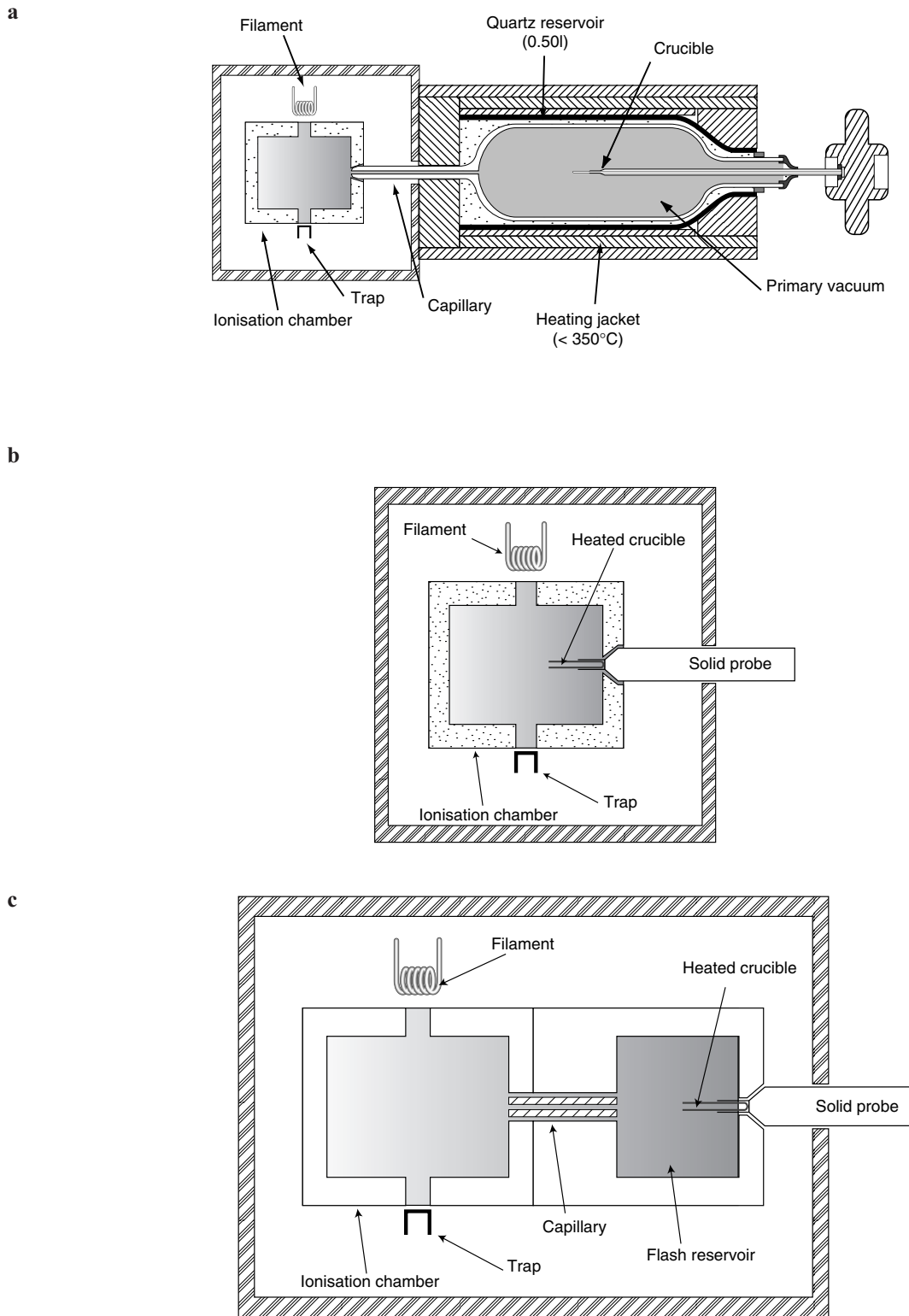


Figure 3

Diagram of the various inlet systems. a: batch inlet system; c: solid probe; d: mini reservoir.

of the batch system lies in that it generates constant flow of the mixture for quite a long time (approximately 30 min) as shown on the total ionic current (TIC) graph against time (Fig. 4a). This enables to acquire several significant spectra with quite a slow scan rate (10 to 30 s/decade) in order to obtain good accuracy when determining exact masses. In such a case, each spectrum is representative of the sample. But with this system, it is rather difficult to control the vacuum/temperature ratio of the reservoir and of the transfer line in order to ensure complete and repeatable vaporisation, without any background effect and without clogging the molecular leak. Vaporisation of the heaviest compounds is not controlled.

The second system (Fig. 3b), called “solid probe”, consists in placing the sample in a crucible. The latter is located at the end of a probe which, via a primary vacuum lock, is inserted up to the ion source. The tip of this probe is then temperature-programmed thanks to a heating resistor. The products are thus vaporised directly into the electron beam. The advantage of this system is to enable very good vaporisation, even of the heaviest compounds since it is possible to heat up to 650°C, under secondary vacuum, the sample which is located in the ion source. Conversely, vaporisation is performed very rapidly (a few seconds) because of the thermal contact with the source whose temperature is close to 330°C (Fig. 4b). It is therefore necessary to adopt a scan rate which is much faster than with a batch system (approximately 0.5 s/decade) and that over a very wide mass range (40-1000), which may be detrimental to the determination accuracy of the exact masses. This system enables to conduct pseudo-distillation of the mixture. It is thus necessary to average all the spectra collected during vaporisation in order to obtain a spectrum representative of the petroleum cut analysed.

2.2 The Enhanced System

A new, hybrid, system (Fig. 3c) has been developed for *IFP* by *Fisons* which combines the advantages of both previous techniques without suffering from their shortcomings.

It consists of a small reservoir (a few millilitres), covered with gold, heated to the same temperature as the source and placed in direct contact with the ionisation chamber. It is therefore under secondary vacuum. The sample, deposited in a crucible, is vaporised in this reservoir thanks to the solid probe. Molecule transfer from the reservoir to the electron beam is performed thanks to a very short, approximately 1 cm, quartz capillary. The main advantage is the easiness with which the samples can be vaporised since, on the one hand, they are under secondary vacuum and, on the other hand, the crucible can be heated directly to 650°C. The second advantage is that the reservoir, even if of small capacity, behaves like a buffer space and slows down the molecule flow towards the ion

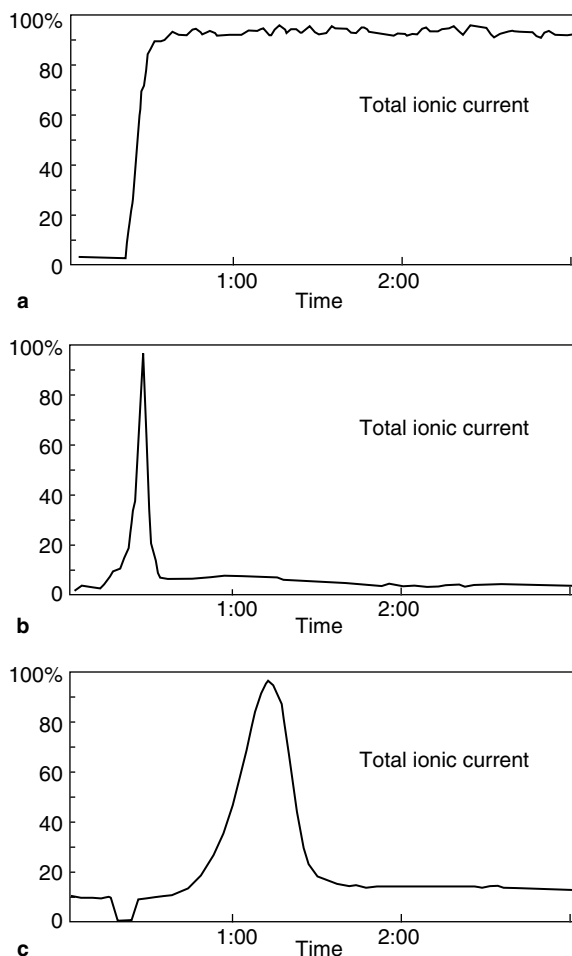


Figure 4

Total ionic current (TIC) of a heavy cut. a: batch inlet system; b: solid probe; c: mini reservoir.

source (Fig. 4c), thus enabling to use slower scan rate, more compatible with good accuracy when determining the exact masses. Moreover, the “background” effect problems are significantly less important since the reservoir is placed under secondary vacuum.

3 OPERATING CONDITIONS

3.1 Mass Spectrometry

This development took place on a high resolution Ultima spectrometer manufactured by *Fisons*. Molecules are ionised by electronic bombardment at 70 eV. The source temperature is 330°C in order to limit the background effects without initiating any cracking. The mass range analysed covers 40 to 1000 a.m.u. The scan rate is 1 s/decade in order

to keep good mass accuracy as well as satisfactory result repeatability. The resolution is 10 000 in order to separate the multiplets of identical mass rating.

The solid probe is programmed from 150°C to 650°C at 50°C/min. The average of all the spectra collected during vaporisation is computed in order to obtain the spectrum representative of the sample on which the quantification calculation will be applied.

Before inlet, the sample is diluted to 1/100th in dichloromethane after homogenisation.

Good adjustment of these conditions is controlled thanks to a 375-450°C test sample whose saturated/aromatic compound balance (as determined by liquid phase chromatography) is 60/40. Its sulphur ratio is 1.09%, i.e. approximately 10% sulphured molecules.

3.2 Liquid Phase Chromatography

After precipitation of the asphaltenes (As) at 80°C *n*-heptane and filtering on Millipore HQ 0.45 µm filter, 0.5 to 1 g sample, diluted in *n*-heptane, is injected via a 4 ml loop, on a column (diameter: 9.53 mm) filled with silica (*Davidson Chemical*) and alumina (Alumina 90 supplied by *Merck*). The saturated compounds (S) are eluted with *n*-heptane for 37 min, the aromatic compounds (A) by an *n*-heptane/toluene mixture (70/30 v/v) for 3 h and the resins (R) by a toluene/dichloromethane/methanol (1/1/1 v/v) for 1 h. The flow rate of the column is 2 ml/min. Silica and alumina are activated a whole night at 180°C and conditioned in the column for 30 min, under *n*-heptane flow. Each fraction collected is vaporised under nitrogen flow and the S/A/R/As distribution is given by weighing.

4 VALIDATING THE INLET SYSTEM

4.1 *n*-Alkanes Analysis

A series of *n*-alkanes, nC_{40} , nC_{50} , nC_{60} has been analysed, in order to prove the good vaporisation of high boiling point compounds. Good vaporisation means that the compound is detected correctly, without any thermal cracking nor background effect. Figure 5 represents the total ionic current (TIC) in relation to the temperature of the solid probe for each paraffin. It shows that compounds whose boiling point is equal to 600°C, can be vaporised correctly, without any cracking, since the temperature of the probe as well as that of the reservoir are always lower than 350°C (limit of crackability temperature) when the product is vaporised. On the other hand, mass spectra do not exhibit any olefin fragment, which would be the signature of thermal cracking.

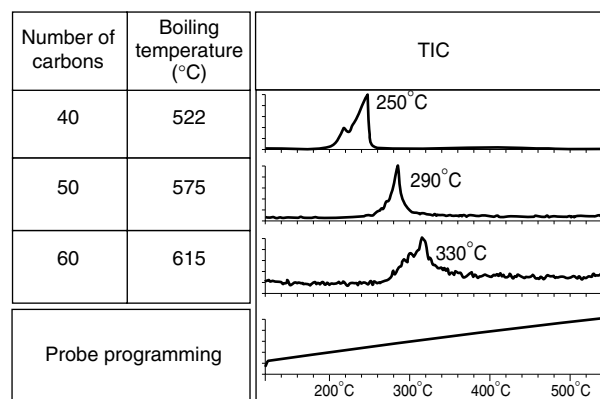


Figure 5
Analysis of *n*-alkanes.

4.2 Analysis of 350-550°C Cuts

In order to validate group-type analyses, the results obtained on 350-550°C cuts, with varied aromatic hydrocarbon contents, have been compared with those of liquid chromatography (LC) which provides the balance between aliphatic hydrocarbons and aromatic hydrocarbons (S/A). The saturates content, determined by liquid chromatography, is corrected by an amount corresponding to the contribution of the resins (and of the asphaltenes, if the latter are present), i.e. it is brought back to 100% (saturates + aromatics) compounds. Indeed, as explained in Section 1, resins and asphaltenes are not taken into account in the MS method since they do not match any quantified class: these are heteroatomic molecules (S, N, O, etc.) whereas solely pure hydrocarbons or sulphured aromatic compounds are quantified.

Aliphatic hydrocarbon content of these petroleum test-cuts ranges from 50 to 80% m/m and their resins content from 4 to 11% m/m. The results of the comparison are reported in Table 2 and show that the S/A balance determined by MS is equivalent to that found by liquid chromatography, although slightly offset. We shall see in the following paragraph that this bias can be explained by the presence of the resins.

4.3 Analysis of 350+ Cuts – Influence of Resins and Asphaltenes

Cuts, previously distilled below 350°C (350⁺) were analysed in order to proceed with this validation. They were selected to cover a wide range of saturated hydrocarbon, sulphur, resins content, and T_{95} as shown on Table 3. They came either from catalytic cracking cuts or from hydrotreating process effluents.

TABLE 2

Comparison of the results of mass spectrometry (MS) and of liquid chromatography (LC) on 350-550 cuts

%m/m	Sample 1		Sample 2		Sample 3	
	MS	LC	MS	LC	MS	LC
Saturated compounds	52.8 ± 2.6	54.0 ± 1.5	71.4 ± 2.8	73.8 ± 1.9	76.0 ± 2.9	81.0 ± 2.0
Aromatic + sulphured compounds	47.2 ± 2.5	46.0 ± 1.3	28.6 ± 2.3	26.2 ± 1.5	24.0 ± 2.0	19.0 ± 1.5

TABLE 3

Characteristics of the samples studied (cuts 350⁺)

	Min.	Max.
Saturated (%m/m)	20	98
Resins (%m/m)	0.3	20
T_{95}^* (°C)	550	710
% sulphur (%m/m)	< 0.1	2

* temperature at which 95% m/m of the product is distilled

Comparison with liquid chromatography is given at Table 4. Figure 6 represents the aliphatic hydrocarbon content generated by MS in relation to the aliphatic hydrocarbon content as determined by liquid chromatography. It shows that MS/LC correlation is not perfect and that certain items deviate from the parity line. This leads to studying the influence of the resins.

If we consider that these are very high boiling temperature and very polar molecules, we may think that they are not vaporised, hence ionised by the electron beam. With this hypothesis, the resulting mass spectrum is representative of 100% of the fraction (S + A) and should be equivalent to the mass spectrum of the fraction (S + A) introduced without resin. In order to check this hypothesis, some samples were first of all separated by liquid chromatography into saturated compounds/aromatic, compounds/resins/asphaltenes and the “saturated” and “aromatic” fractions were remixed and analysed by mass spectrometry.

The results of this comparison can be seen at Table 4 and show that for some samples, there are differences with the analysis of the total product. Figure 7 represents the ratio of saturated compounds as determined by mass spectrometry of the fractions S + A in relation to the ratio of saturated compounds (corrected according to the contribution of the resins) given by liquid chromatography. It shows that MS/LC correlation is better when the resins are absent and that we obtain, while taking relative errors of both techniques into account, satisfactory matching. The sole items deviating from the parity line correspond to samples whose final boiling point is higher than 600°C. Poor vaporisation is then responsible for this bias. This confirms the scope of this inlet system, already defined using *n*-alkanes.

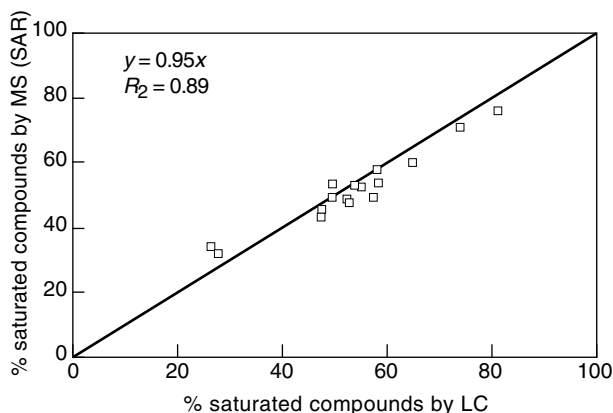


Figure 6

Correlation between the % of saturated compounds determined by liquid chromatography (LC) and by MS on the total samples.

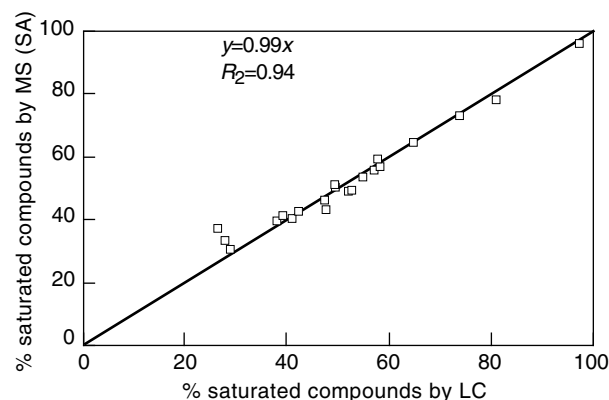


Figure 7

Correlation between the % of saturated compounds determined by liquid chromatography (LC) and by MS on the fractions S + A.

It is therefore possible to conclude that some resins are surely vaporised and that they have an impact on the results by the presence of fragments interfering with those of the quantified group-types. For example, the alkyl chains must obviously generate fragments typical of the paraffins and this contribution is not taken into account in the calculation

TABLE 4
Comparison of liquid chromatography and mass spectrometry results

Saturates by liquid chromatography (%m/m)	Saturates by mass spectrometry on total sample (%m/m)	Saturates by mass spectrometry on SA (%m/m)	Resins + asphaltenes (%m/m)	Sulphur (%m/m)
26.4	34.2	34.7	17.7	2.0
27.9	32.0	33.4	20.0	2.0
28.8	n.d.	30.6	17.1	1.7
38.1	n.d.	39.8	11.2	0.4
39.1	n.d.	41.0	6.7	0.2
41.0	n.d.	40.4	10.2	0.2
42.2	n.d.	42.7	8.5	0.1
47.3	43.6	46.0	8.0	1.3
47.4	45.3	46.2	5.9	1.8
47.6	45.7	43.2	4.6	1.9
49.4	53.5	50.7	4.5	0.9
49.5	49.2	50.5	9.2	1.1
52.4	48.9	49.3	5.4	1.5
52.8	48.0	49.2	6.1	0.2
54.0	52.8	n.d.	5.1	0.1
54.8	52.9	53.7	8.0	0.5
57.1	49.6	55.8	6.8	1.9
58.1	57.9	59.2	5.8	0.7
58.3	53.8	57.2	10.4	0.7
64.8	60.2	64.5	5.1	0.5
73.8	71.4	n.d.	3.9	0.4
81.0	76.0	78.0	11.0	0.1
97.3	n.d.	96.0	0.3	<0.1

TABLE 5
Accuracy of the method

	Sample 4		Sample 5	
	Average value	* CI _R	Average value	* CI _R
% saturated compounds	79.9	2.9	47.3	2.5
% total aromatic compounds	18.2	1.9	34.3	2.3
% monoaromatic compounds	9.3	1.1	11.5	1.3
% diaromatic compounds	5.2	0.8	8.8	1.1
% triaromatic compounds	2.1	0.5	5.7	0.8
% sulphured aromatic compounds	1.9	0.5	18.4	2.0

* CI_R: intralaboratory reproducibility confidence interval.

matrices unlike the contribution of the alkyl chains of the other group-types of pure aromatic or sulphured compounds.

Conversely, there is no correlation between the resin ratio of the sample and the deviation between the saturated ratio determined by liquid chromatography and mass spectrometry. It would seem that their structure was more important than their presence. Little resins in small quantities can be vaporised and disturb the results whereas larger resins could not be injected into the ionisation source and will therefore exert no influence, whatever their contents. Analysis of resins, on their own, has enabled to verify this hypothesis. They are partially vaporised and the resulting quantitative analysis shows the presence of fragments, which interfere predominantly with aromatic compounds.

This means that, as we are unable to anticipate their behaviour, it is necessary to extract resins and asphaltenes from the 350⁺ cuts before analysing them.

4.4 Fidelity

Table 5 gives the estimates of the intralaboratory reproducibility confidence interval (CI_R) of the method, determined thanks to two samples, one with 80% m/m and the other 47% m/m saturated hydrocarbons. Ten doubled analyses were carried out on each sample (one double per day), over a two-month period in order to take into account time variations due to adjustments and to the ageing of the spectrometer source.

CONCLUSION

Analysis of heavy petroleum cuts (350⁺) is a necessary condition of optimising validation processes of vacuum distillates and of residues. With a view to characterising these products in a detailed manner, the mass spectrometry chemical group-type analytical protocol has been enhanced. The main objective of this development consisted in optimising the sample inlet system, a system that enables to vaporise molecules into the source of the spectrometer. Numerous fruitless trials, using the accessories available on the market, have been performed. They have led to the

design of a new vaporisation system, which combines the advantages of the other inlet modes without suffering from their shortcomings.

The study of *n*-alkanes with 40, 50 and 60 atoms of carbon has shown that the samples are vaporised correctly until a final boiling point of 600°C, i.e. the whole product is vaporised without any cracking nor residual spectrum.

The quantification properly speaking, was validated by comparison of the values of the saturated hydrocarbons/aromatic hydrocarbons balance, as determined by mass spectrometry, with those given by liquid phase chromatography. This comparison has shown that it is necessary to extract the resins and the asphaltenes from the samples before any analysis since these compounds distort the results when they are vaporised, thereby generating fragments which interfere with the characteristic fragments of the quantified group-types.

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