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Quantitative Hydrocarbon Group Type Analysis of Petroleum Hydroconversion Products Using an Improved TLC–FID System

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Abstract

This work deals with the study of an improved thin-layer chromatographic–flame-ionization detection (TLC–FID) system (using the newer configuration of the detector, an automatic sample spotter, and a careful selection of the operating parameters) in the quantitative hydrocarbon group type analysis of a deasphalted heavy oil from petroleum and its derived hydrocracking products. The separation method proposed allows for the detection and quantitation of saturates, alkylaromatics, aromatics, polars, and an uneluted fraction. The repeatability of the experiments has always been better than that of the ASTM D2007 standard for each fraction. It is not affected by application volumes or concentration in the studied ranges. Results from the absolute calibration method and from a variety of the internal normalization procedures are comparable, although the latter is faster and allows a rapid determination of the linear range of the detector. Factors such as eluent development length or application spot size do not influence the FID response of our samples under the studied conditions. Likewise, the behavior of the detector is linear with mass in the range studied for each separated fraction.

Introduction

Hydrocarbon group type analysis (HGTA) is currently used to study the variables that influence the different petroleum and conversion processes because hydrocarbon groups rather than individual molecules determine the chemical behavior of complex petroleum or coal products. The usual techniques for direct HGTA have important limitations, as has been reported (1,2). Solvent fractionation techniques are less selective than chromatographic ones. However, gas chromatography (GC) is limited because of the involatility of some compounds. Liquid chromatographic (LC) techniques are lengthy, tedious, and laborious, and they require considerable quantities of solvents. The columns need to be repacked for each determination, and the recovery of the fraction is incomplete (3,4). Furthermore, LC techniques involve materials and solvents that interact with the components of samples. Besides these disadvantages, the American Society for Testing of Materials (ASTM) D2007 standard, an LC-based method, requires removal of asphaltenes prior to use (5). Likewise, high-performance liquid chromatography (HPLC) presents problems with regard to the irreversible adsorptions of polar compounds, which provoke column deterioration and quantitation problems using conventional HPLC detectors (6,7). The coupling of HPLC with mass spectrometry requires the use of sophisticated interfaces and is still being developed (8). Another chromatographic technique, thin-layer chromatography (TLC) with ultraviolet detection, also presents problems in quantitation.

TLC with flame-ionization detection (FID), namely Iatroscan (Iatron Labs; Tokyo, Japan), combines the resolution efficacy of TLC and the possibility of quantitation by FID. A book (9) and several reviews (10,11) were published on this technique; they were mostly applied to other fields of chemistry (mainly lipids). An application to petroleum and coal was also reported during the 1980s (12). TLC–FID was claimed to be a rapid, reproducible, and quantitative technique adequate for rapid quality control and applicable to the whole sample without any preseparation. However, some doubts as to the acceptability of the quantitative results with this instrument were recently reported (11). This is not surprising for several reasons. First of all, there have been changes in the configuration of the detector in the newer models (Mark IV, Mark 5) with respect to the older ones (Mark II, III, TH-10) (10). Moreover, the sensitivity of the electronics in the data acquisition systems has been improved in the last decade. Also, the application of the sample proved to be a major factor with regard to reproducibility and quantitation in TLC–FID (11). Many results were reported using different detector configurations, inadequate spot systems, and different data acquisition systems.

Apart from these factors, there are other variables that influence the FID Iatroscan response, including the chemical structure of the components of the sample, the amount of sample spotted, the scan speed, and the hydrogen and air flows, as was extensively described by Ranny (9). A proper choice of these variables is needed to use this instrument accurately. However, some points need further verification, such as the re-

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ported variation of the FID Iatroscan responses with the shape of the peak; clarification of the different processes involved in FID scanning is also necessary.

In a recent review, Shanta (11) observed that it would be useful if users of the newer model of Iatroscan provided information on the reproducibility and linearity of response that can be obtained with the instrument because of the scarce data available in the literature. In this context, the aim of the work presented here is to test the TLC–FID technique in performing a quantitative HGTA of a heavy petroleum residue and a set of its derived products from catalytic hydrocracking by using the newer configuration of the FID Iatroscan detector and an automatic sample spotter and by carefully selecting the setup and calibration variables. This paper also clarifies some aspects of the Iatroscan FID response, assesses the linearity of the detector, and evaluates the possibility of using different calibration methods for quantitative purposes.

Experimental

Products analyzed

A set of samples consisting of a heavy petroleum residue and its derived products from catalytic hydrocracking (using different catalysts) was analyzed by TLC–FID.

A study of the repeatability of experimental results using TLC–FID, a choice of standard conditions of analysis, and calibration were carried out using the hydrocracking feed, which was an *n*-butane-deasphalted oil (DAO) obtained from a 450+ Brent vacuum residue. A summary of its properties is given in Table I.

The results of this study were directly applied to the quantitative analysis of several catalytic hydrocracking products derived from DAO and obtained at the Institut de Recherches sur la Catalyse (CNRS; Villeurbanne, France) under the following conditions: temperature, 440°C; time, 1 h; and pressure, 14 MPa of initial H_2. A batch reactor heated by induction was used. The procedure was detailed elsewhere (13). Several highly dispersed, disposable catalysts at low concentrations (450 ppm metal) were utilized. They were produced in situ from the following precursors: a molybdenum naphthenate (Shepherd Chemical); NiMo–Al_2O_3 (Shell 424 catalyst); and a nickel plasma solid, which was produced by means of an electrical discharge spark between two nickel electrodes immersed in a hydrocarbon. The product obtained in the absence of a catalyst was also analyzed. Details about preparation and characterization of this catalyst were already published (14).

Table I. Physicochemical Properties of an *n*-Butane Deasphalted Oil

Atomic H:C ratio	1.64
Total sulfur (wt %)	0.85
Nickel + Vanadium (ppm)	5.2
510+ distillation fraction (%)	95
Viscosity (cst)*	60
Density (g/cm)†	1.058

* At 100°C
† At 15°C

TLC–FID experiments

An Iatroscan Mark 5 TLC–FID apparatus (Iatron Labs) was used for the chromatographic separation and quantitation of the peaks.

Chromatographic separation was carried out on Chromarods-SIII, which consisted of a thin adsorbent layer (75 µm) formed on the surface of a quartz rod (15.2 × 0.9-mm i.d.) by sintering inorganic binders together with silica gel (particle size, 5 µm; pore diameter, 60 Å). In a usual experiment, a set of 10 chromarods was preassembled in a frame; after application of the sample and subsequent development with solvents, they were sequentially passed at a constant speed through the H_2 flame of an FID for quantitation of the peaks. The Mark 5 Iatroscan model includes the newer detector (FID) configuration in which the ion collector is closer to the chromarods than it was in the older models (Mark II, III, IV, and TH-10). It was reported to be more sensitive and to give better reproducibility (11).

A pure hydrogen flow of 160 mL/min and an air flow of 2.1 L/min were used in our experiments as in previous experiments (9).

Acquisition and treatment of TLC–FID data were carried out using a data acquisition card and Boreal software (JMBS Development; Grenoble; France). Several experiments required different data processing. Raw chromatograms were exported to a computer worksheet in ASCII form, and a manual integration by *y*-summation was performed. This procedure allowed detection of saturated signals and complete control of integration. No differences were observed between the worksheet and Boreal software integrations.

Concerning the application of sample, finer, more reproducible spots were obtained using automatic sample spotters rather than manual application systems (11). A 2-µL syringe was used with one of these autospotters (Model 3202/IS-02, SES; Germany). Samples were solubilized in CH_2Cl_2 (approximately 10 mg/mL). They were freshly prepared or stored under argon in a freezer for reapplication. Volumes between 0.5 and 2 µL were usually applied on the chromarods, and development was carried out according to an increase of polarity using *n*-hexane, toluene, and CH_2Cl_2–methanol (DCM–MeOH) (95:5, v/v) as eluents (analytical grade, Scharlau; Barcelona, Spain). The addition of a 5% volume of methanol to the polar solvent (DCM) was found to have an advantageous effect in mobilizing polar material away from the origin of the chromatogram (15). In this case, fresh eluent was prepared daily. Incomplete drying of the chromarods prior to FID scanning (after the develop-

Table II. Position Repeatablity

	Peak 1		Peak 2		Peak 3		Peak 4	
	t_R*	SD*	t_R	SD	t_R	SD	t_R	SD
Frame 1	0.18	–	0.29	–	0.39	–	0.47	–
Frame 2	0.18	–	0.29	–	0.39	–	0.47	–

*Abbreviations: t_R, retention time in minutes; SD, standard deviation.

ment) was reported to produce a high noise level during detection. Therefore, drying was carried out at 110°C (toluene's boiling point) for 5 min.

A high speed (30 s/scan) was used to scan the samples. High velocities were found to produce higher responses (9,16) and improved reproducibility (9). The scan speeds of the Mark 5 range from 25 to 60 s/scan. A speed of 30 s/scan was used instead of 25 s/scan because this allowed comparison with other results in the literature. At this velocity, the temperature of the chromarod surface should not be so high as to prematurely volatilize the products (17).

The complete combustion of all components of the samples was verified by running blanks after scanning and using the origin scan mode of the Mark 5, which performs additional scans of each chromarod around the origin.

In order to define a strict operating procedure, the first step in our research was to study some factors that influence the repeatability of the experiments. This will be detailed in the Results and Discussion section. As a consequence, the following operational procedure was adopted: two blank scans to remove contaminants on the rods before application of sample; 5-min stabilization or cooling in a constant humidity chamber (65% humidity) (18); spotting of sample; 10-min presaturation in the *n*-hexane development tank; development with *n*-hexane; 2-min drying at 110°C; 10-min presaturation in the toluene development tank; development with toluene; 2-min drying at 110°C; 10-min presaturation in the DCM–MeOH (95:5, v/v) development tank; development with DCM–MeOH (95:5, v/v); 5-min drying at 110°C; 5-min stabilization or cooling in the constant humidity chamber; and scanning of the chromarods.

Medium-pressure liquid chromatography

The DAO was submitted to medium-pressure liquid chromatography in a preparative Quickfit column (50 cm × 10-mm i.d.) using silica gel (70–230 mesh ASTM, Merck; The Netherlands) as a stationary phase in order to separate pure fractions to calibrate the Iatroscan TLC–FID.

Silica gel was previously activated for 12 h at 105°C and then deactivated with 4 wt % water. The introduction of the sample was carried out as follows: 1.75 g DAO was solubilized in a minimum amount of DCM and preadsorbed onto $CaCO_3$, and subsequently, the solvent was removed in a vacuum oven at 30°C overnight. The resulting powder was introduced onto the top of the silica gel column, and solvents (*n*-hexane, toluene, and DCM, in order) were eluted by using a Duramat pump. The initial flow of eluent was 10 mL/min. Subfractions were collected. Further removal of solvents was carried out for each subfraction in a rotary evaporator, then using N_2 at room temperature, and finally in a vacuum oven at 40°C. Each subfraction was analyzed by Iatroscan TLC–FID using the same conditions as those selected for the whole samples in order to monitor the chromatographic elution and verify the purity of the separated fractions.

Fourier transform infrared (FTIR) spectra of the chromatographic fractions were recorded on a Magna 550 Nicolet spectrophotometer using NaCl windows. The GC–FID analysis was carried out using a Varian Model 344 apparatus under the following conditions: column, polymethylsilane (25 min); initial temperature, 50°C (5 min); final temperature, 300°C; temperature gradient, 5°C/min; injector temperature (split mode), 300°C; detector temperature, 250°C. Similar chromatographic conditions were applied in the GC–MS analysis of the same fraction using a Hewlett-Packard Model 5890 chromatograph (Wilmington, DE) and a Model 5972 mass selective detector.

Results and Discussion

Repeatability of TLC–FID Iatroscan experiments

Repeatability was defined as the difference between two test results obtained with the same apparatus under constant operating conditions on identical test material (DAO), even with different operators (5).

As a starting point, a sequence reported in the literature (18) for samples similar to those studied here was adopted (*n*-hexane, 10 cm; toluene, 5 cm; and DCM–MeOH [95:5, v/v], 2 cm). A single determination was defined for these experiments as the average result from five chromarods, according to the work of Ray and co-workers (15) (Tables II and III).

In this procedure, some minor factors that influence the operating mode in Iatroscan must be considered:

- The elution length is difficult to control in spite of the use of a rod viewer. A strict control of time is necessary to assure repeatability of retention times. This was already observed by Karlsen and Larter (16). Thus, the previously mentioned sequence is equivalent to the following: *n*-hexane, 19 min; toluene, 7 min; DCM–MeOH (95:5, v/v), 1.5 min.
- After development with the procedure

Table III. Integration Repeatability

	Peak 1	Peak 2	Peak 3	Peak 4
Frame 1				
Average % area (n = 5)	33.22	53.39	12.89	0.50
Standard deviation	0.51	0.60	0.16	0.07
CI* 95%	33.85–32.58	54.13–52.65	13.08–12.69	0.59–0.41
CI 99%	34.27–32.17	54.62–52.17	13.21–12.56	0.65–0.35
CI 99.9%	35.18–31.25	55.69–51.10	13.49–12.30	0.78–0.21
Frame 2				
Average % area (n = 5)	31.74	53.33	13.60	1.61
Standard deviation	0.45	0.58	0.36	0.13
CI 95%	32.30–31.17	54.05–52.61	14.10–13.11	1.79–1.42
CI 99%	32.67–30.80	54.52–52.14	14.43–12.78	1.90–1.30
CI 99.9%	33.48–29.99	55.55–51.11	15.15–12.06	2.17–1.04

* The confidence interval ($CI = Xm \pm t \times s/\sqrt{n}$) is defined here as the interval in which the true value lies with a given probability, where Xm is the average area percent, t is the Student's distribution, s is the standard deviation, and n is the number of measurements.

detailed in the Experimental section, chromarods can be stored before scanning for an indefinite period of time in the constant humidity chamber. No changes were observed for storage times of up to 2 days.

- The application of different sample volumes (0.5–2 µL) or drying between eluents did not affect the repeatability parameters. Drying was preferred to not drying because peaks were better formed in this case.

Tables II and III show some intraframe and interframe duplicate experiments of repeatability. Chromatograms are shown in Figure 1.

Retention times were repeatable either for the chromarods of a same frame or for interframe runs, regardless of the spotting volume (1, 1.5, or 2 µL) (Table II).

Variations in the standard deviation for the direct integrations of twin peaks with retention times (t_R) of 0.26 and 0.31 min (reported as aromatics) can be attributed to a bad separation of the sample using this sequence. Standard deviation for peaks 1 (t_R, 0.18 min, reported as a saturate) and 3 (t_R, 0.39 min, reported as a resin) were comparable for these runs (Table III).

Similar conclusions were obtained for another development sequence (*n*-hexane, 38 min; toluene, 7.5 min; DCM–MeOH [95:5, v/v], 1.5 min) using two application volumes (1.5 and 2 µL).

When using the selected procedure properly, repeatability was not affected by changes in the laboratory atmosphere. However, when comparing these results with a replica of the same experiment but using a stabilization chamber with the introduction of ambient air, retention times with standard deviations not equal to zero were observed for the chromarods nearer to the air inlet, and higher standard deviations for the area percentages were also found.

Improving the separation

The development sequence used ("short"; hexane, 19 min; toluene, 7 min; DCM–MeOH, 1.5 min) did not give a good separation of DAO. Two unresolved peaks were obtained in the aromatic region (18). For this reason, other sequences were investigated to improve the separation (Figure 2). As a result, the following sequence was adopted as the standard for the analysis of our hydrocracking products: hexane, 38 min; toluene, 3 min; and DCM–MeOH, 30 s (Figure 2D).

Regardless of the sequence used, five peaks were obtained. Furthermore, the only effect of increasing the development length in the case of *n*-hexane and increasing the differences in the development length between *n*-hexane and DCM–MeOH was the better or worse distribution of the aromatics in two peaks whose separation depended on the particular sequence selected. It did not affect the percentage of areas of the other peaks.

In order to know which eluent developed peak 2 in the standard sequence (Figure 2D), three chromarods of a frame were developed using only *n*-hexane (38 min), and then they were scanned. Subsequently, the next three chromarods were developed with *n*-hexane (38 min) and then with toluene (3 min). They were also scanned. Finally, the last four chromarods of the frame were developed with the complete standard sequence. It was demonstrated that peaks 1 (t_R, 0.10 min) and 2 (t_R, 0.19–0.26 min) were developed with *n*-hexane; peak 3 (t_R, 0.37 min) was developed with toluene; peak 4 (t_R, 0.43 min) was developed with DCM–MeOH; and peak 5 (t_R, 0.47 min) corresponded to uneluted products. This standard sequence

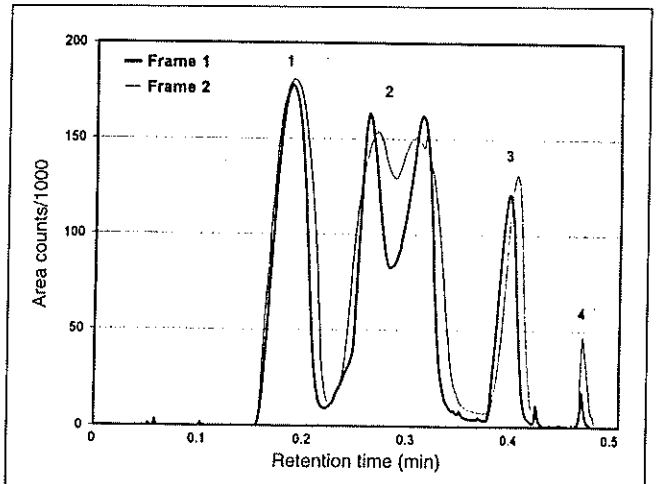

Figure 1. Interframe and intraframe TLC–FID experiments using the short sequence (hexane, 19 min; toluene, 7 min; and DCM–MeOH, 1.5 min). Peaks: 1, saturates; 2, aromatics; 3, resins; 4, uneluted.

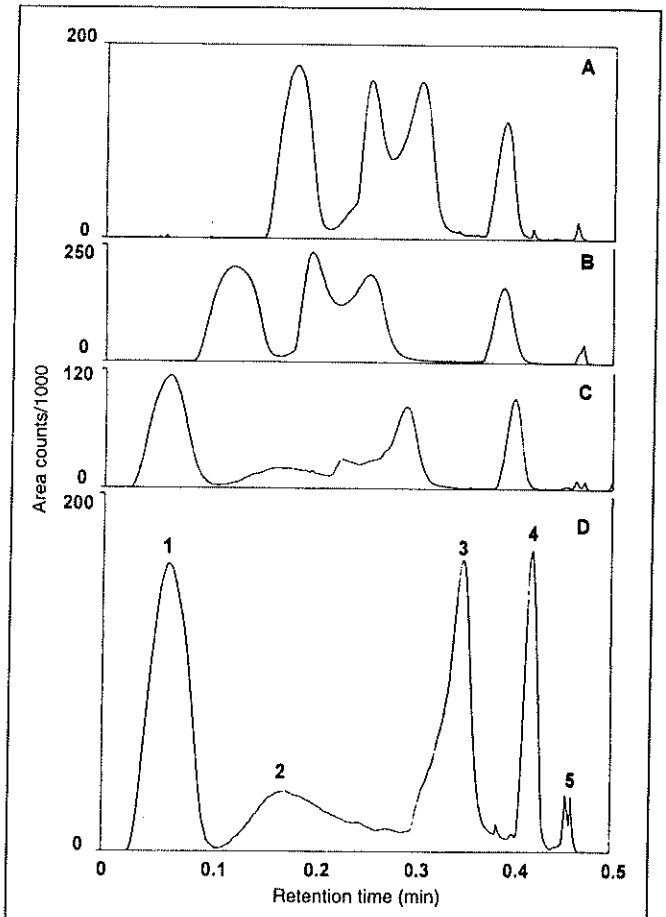

Figure 2. Some TLC–FID development sequences used to improve the separation. Sequence A: hexane, 19 min; toluene, 7 min; DCM–MeOH, 1.5 min. Sequence B: hexane, 28.5 min; toluene, 10.5 min:; DCM–MeOH, 1.5 min. Sequence C; hexane, 38 min; toluene, 7.5 min, DCM–MeOH, 1.5 min. Sequence D; hexane, 38 min; toluene, 3 min; DCM–MeOH, 30 s.

gave an adequate separation between the peaks, although peak 2 showed some tailing, which led to a shoulder in peak 3.

Calibration and quantitation

Quantitative HGTA of fossil fuels has been carried out using several approaches, including those described by Ranny (9). Assuming that all peaks give the same FID response, direct area-count normalization has sometimes been used as a direct measure of the fraction mass percentages (15). However, FID response is known to depend on the chemical nature of the peaks; therefore, this hypothesis needs further verification. In order to calibrate FID peak response, two different methods are possible. One method involves absolute calibration using external standards (12). In this case, different amounts (micrograms) of each standard were plotted versus response, which is defined as area counts (μV/s). For fossil fuel products, pure fractions derived from LC are the most adequate standards to carry out the calibration. The second method is one in which the responses of the different peaks are plotted together versus different amounts (micrograms) of the whole sample.

Method 1 seems theoretically obvious, has been frequently used (12,18,19), and allows a direct characterization of the LC fractions, but it is lengthy, tedious, and requires a large quantity of reactives. However, it allows for the possible use of nonlinear calibration relationships. Method 2 does not depend on any external additional technique, and it is fast and theoretically equivalent to the previous one. However, it is not as intuitive, has not been sufficiently explained in the literature (20), and hence has been less frequently used. A direct comparison of the two methods was undertaken.

The LC of DAO was carried out in order to study Method 1. Iatroscan also proved to be a useful and rapid off-line tool to monitor the elution and verify the purity of the separated fractions.

In LC, the eluted fractions (or subfractions) of a set of products are usually collected on a volumetric basis previously determined for a standard sample. However, determination of the elution volumes needed to isolate each fraction is sometimes too delicate for a given sample. In our case, several tentative LC runs were made. In one of them, subfractions were collected every 100 mL of eluent. In this case, TLC–FID demonstrated that aromatics already coelute with saturates in the first subfraction of *n*-hexane. When an excess of *n*-hexane was used, even polar compounds were eluted, in spite of the light yellow color of the *n*-hexane eluate (Figure 3). Strict control of the elution volumes can be achieved using TLC–FID. In another attempt, subfractions were collected every 10 mL. Figure 4 shows a schematic example concerning the evolution of the elution. Pure fractions (greater than 99 in area percent) were obtained in the case of peaks 1, 2, and 4. A 95% purity was obtained for peak 3. Each one of these fractions appeared as a unique peak with the same retention time as its corresponding peak in the chromatograms of the whole sample.

The chemical nature of the fractions was studied using FTIR spectroscopy (Figure 5). Peaks 1, 3, and 4 (Figure 2D) correspond to the fractions commonly distinguished. Peak 2 is a result of the improvement obtained in the separation and therefore must be characterized. The fraction corresponding to peak 1 shows a typical spectrum of paraffinic or naphthenic compounds. The heavy character of this fraction was outlined by the impossibility of analyzing it by GC–FID or GC–MS under the conditions described in the Experimental section. The fraction corresponding to peak 4 shows a spectrum with C=O bonds (1686 cm^{-1}) and aromatic stretching at 1606 cm^{-1}. This verifies the polar nature of this fraction. The aromatic nature of the fraction corresponding to peak 3 is highlighted by the presence of aromatic bands (1606 cm^{-1}) and the typical out-of-plane vibration in the zone between 900–700 cm^{-1}. Concerning the fraction corresponding to peak 2, this presents a slight aromatic C–C band. The absorbance ratio ($A_{C-C\ 1600\ cm^{-1}}/A_{C-H\ 2924\ cm^{-1}}$) is clearly lower than that of peak 3. However, the spectrum is similar to that of the saturates. Fraction 2 seems to be composed of saturates (paraffins or naphthenes or both) and a small concentration of aromatic moieties. Based on this information, peaks 1, 2, 3, and 4 will be referred to as saturates, alkylaromatics, aromatics, and polars, respectively. Peak 5, which corresponds to uneluted products, is usually referred to in the literature as asphaltenes.

A linear regression was performed for each one of the fractions (except for the uneluted) in the studied ranges of mass

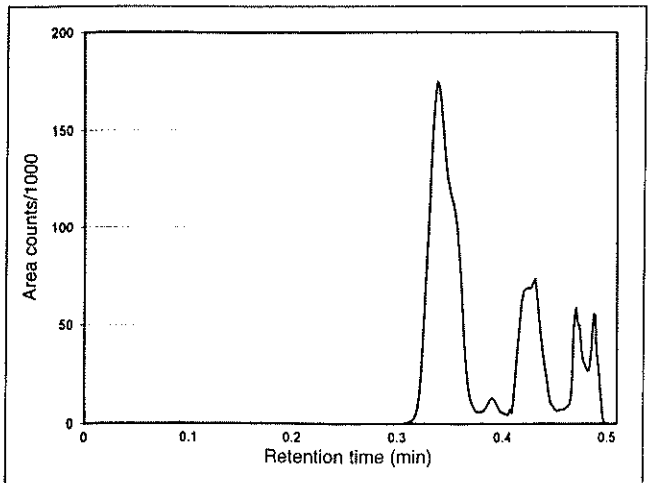

Figure 3. Monitoring a medium-pressure liquid chromatographic elution using TLC–FID. Coelution of aromatic and polar compounds was seen with an excess of *n*-hexane (950 mL).

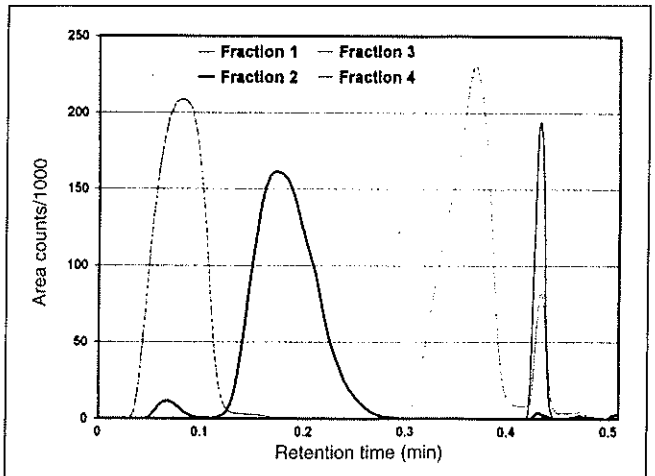

Figure 4. Verification of the purity of medium-pressure liquid chromatographic isolated fractions by using TLC–FID.

(Figure 6). The uneluted fraction was supposed to have the same response as polars because of its chemical similarity (21) and the impossibility of isolating this uneluted fraction. Indeed, uneluted percentages were calculated using the regression of polars. The process of aromatic calibration required a slight change in the procedure because the calibrating fraction contained approximately 5% polar compounds. Therefore, the effective masses of the aromatic fraction were corrected by subtracting the mass of the polar fraction obtained using its corresponding calibration curve.

Correlations were good despite the fact that the points in the curves were indistinctly obtained, varying either in the mass applied (sample concentration) or in the size of the applied spot (application volume ranging from 0.5 to 2 µL).

The mass range studied was between 4.5 and 23 µg for saturates, alkylaromatics, and aromatics. However, it was not possible to spot more than 3.2 µg of the pure polar fraction without saturating the FID. This seems to be a known problem, as can be seen in a figure published by the manufacturers of the apparatus (22); a similar elution sequence and the Mark IV model was used. A tentative explanation of this fact is as follows. When the pure polar fraction is applied and after elution, a fine spot (i.e., a high and sharp peak) is obtained because of the absence of diffusion (as it is located near the origin). According to chromatographic theory, the longer the development takes, the broader the shape of the peak. In the case of polars, the sharpness of the peak causes a very high signal that tends to saturate the detector. This is not a significant problem when analyzing a real sample because coelution with the other fractions gives broader polar peaks, therefore preventing the problem.

Table IV shows the definitive results of the analysis of DAO (in weight percent) after application of the corresponding regressions using both the short and the standard sequences. Averages of 10 chromarods were taken into account. In order to verify the analytical method, two different concentrations of DAO were spotted. The results of Method 1 were coherent. Saturates and polars remained constant using both sequences. The standard sequence allowed for the separation of one more chemical family (alkylaromatics) than the short one; there was only a slightly higher standard deviation and slightly worse repeatability for the aromatics and polars (Table V). However, repeatability was better in all the cases for the Iatroscan experiments as compared with that of ASTM D2007 standard (5) for a given confidence interval (95%), as shown in Table V.

When comparing these results with those obtained from Method 2, it should be noted that this method is based on the fact that whenever the response of the detector to the different fractions is linear and passes through the origin, area percentages can be used directly as mass percentages. A plot of area versus whole sample mass allowed a graphical identification of the linear range for which this assumption can be made. Figure 7 shows these plots in the case of DAO for the standard sequence. A direct inspection of these plots revealed that the previous hypothesis was perfectly assumable in the range 0–10 µg with the Mark 5. When the relationship between linearity and the differences between area and mass percentages (obtained from Method 1) were considered (shown in Table VI), a direct correspondence could be seen. There were bigger differences between area and mass percentages as linearity became worse.

As previously mentioned, DAO was used here as a standard to carry out the HGTA

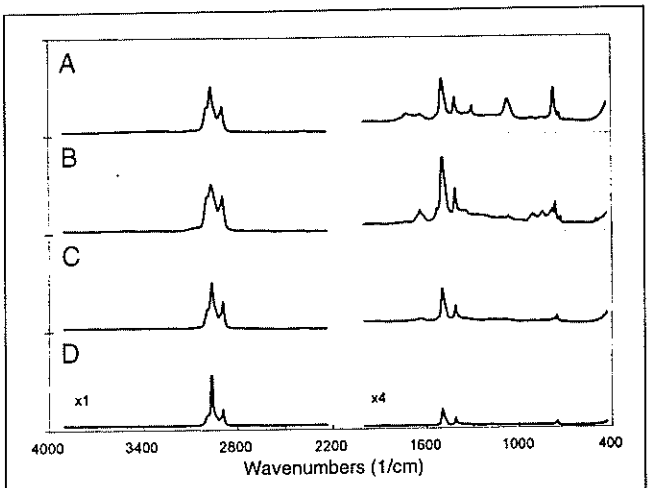

Figure 5. Fourier-transform infrared spectra of a medium-pressure liquid chromatographic fraction: A, polars (TLC–FID; t_R, 0.43 min); B, aromatics (TLC–FID; t_R, 0.19 min); C, alkylaromatics (TLC–FID; t_R, 0.10 min); and D, saturates (TLC–FID; t_R, 0.37 min).

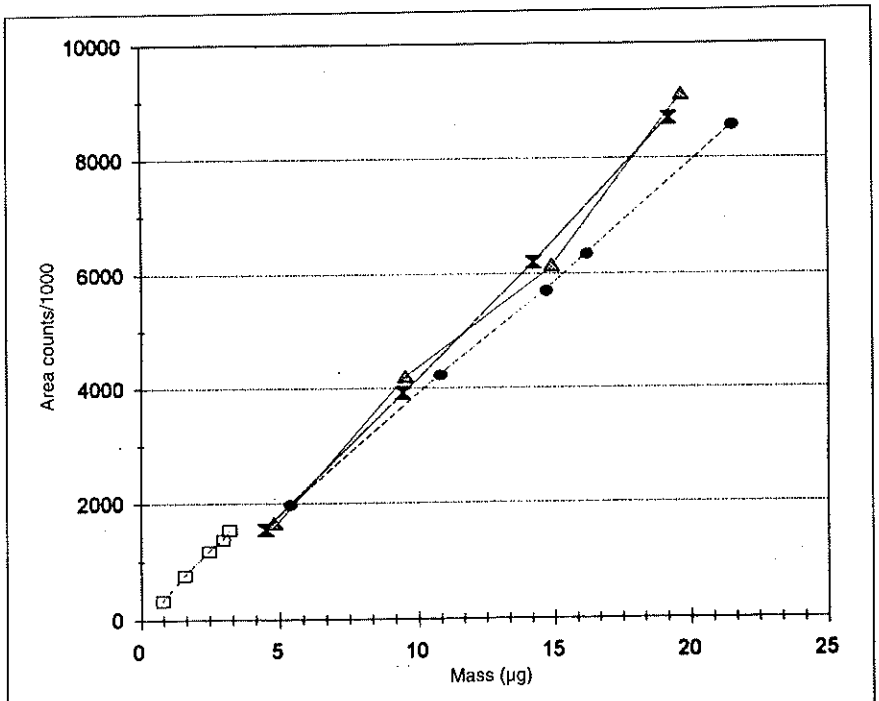

Figure 6. TLC–FID response versus mass of each medium-pressure liquid chromatographic fraction (method 1). Regression coefficients: □, polars, R, 0.9973; ⧗, alkylaromatics, R, 0.9978; △, aromatics, R, 0.9903; and ●, saturates, R, 0.9996.

analysis of a set of its derived hydrocracking products using different catalysts. In spite of its heavy nature (510°C+), it was found to be a good calibrant with regard to the hydrocracking products because the hydroconversion products show the same qualitative composition with identical retention times as DAO in terms of TLC–FID peaks. Table VII shows the results for the hydrocracking products obtained with the standard sequence.

Other aspects of the Iatroscan FID response

The response of polars seemed to be higher than that of the other fractions under the studied conditions. Initially, this could be surprising because FID responses in GC depend somewhat on chemical structure, and it is well established that they decrease if the functional groups or heteroatoms are substituted for hydrogen atoms in hydrocarbons (23). However, conclusions from FID–GC should not be extrapolated to Iatroscan FID because of deep, inherent differences between both systems; these differences are mainly caused by the presence of an initial volatilization step (16). Relative responses of polars and aromatics were reported to vary with the hydrogen flow (16), and the high hydrogen flow rates used in the Iatroscan FID detector (16,24) may have been one of the reasons for the high response of uneluted fractions and polars. Another work (22) reported a slightly lower response for a polar fraction of a vacuum-topped residual oil. However, development conditions were different, and no indication of H_2 flow was given.

The supposed relationship of the shape of the peaks and the response is another interesting factor. The FID response of any lipid class was reported to be affected by the distribution of the sample along the chromarods (10,11,25). According to this theory, the factors that affect the shape (e.g., development length) would have an effect on the response. No explanation has been given for this. Some loss of ionizable material, as well as of uncollected ions, has been considered inevitable (10). A possible nonuniformity of the chromarods along their length was also proposed (11). Although variations from rod to rod within a set were found in the past when chromarods were handmade, the modern S-III chromarods are machine made, and it has been sufficiently demonstrated in the literature that they are uniform and reproducible. In order to clarify this point, the same sample of our pure polar fraction was developed to five different lengths using DCM. In our case, no significant variation of FID response in relation to the development length was found.

Table IV. Comparison of DAO Results*

Sequence	Saturates	Alkylaromatics	Aromatics	Polars	Uneluted
Standard sequence					
Method 1 (% mass)	36.13† (0.71)	19.90 (0.81)	31.17 (1.47)	11.30 (0.48)	1.50 (0.24)
Method 2 (% area)	34.90 (1.20)	18.18 (1.36)	32.38 (1.82)	13.20 (0.83)	1.34 (0.37)
Short sequence					
Method 1 (% mass)	36.18 (0.69)	–	51.88 (0.74)	11.19 (0.25)	0.75 (0.22)
Method 2 (% area)	34.44 (1.35)	–	51.93 (1.65)	13.06 (0.34)	0.57 (0.22)

* Standard deviations in the parentheses. All values are the average of 10 chromarods.

Table V. Mass Range Width for Different DAO Analytical Sequences*

Sequence	Saturates	Alkylaromatics	Aromatics	Polars	Uneluted
Standard	1.02	1.16	2.11	0.69	0.47
Short	0.99	–	1.06	0.36	0.31
ASTM D-2007	2.10	–	2.30	1.20	0.81

* Values are for a given confidence interval (95%). Average of 10 chromarods.

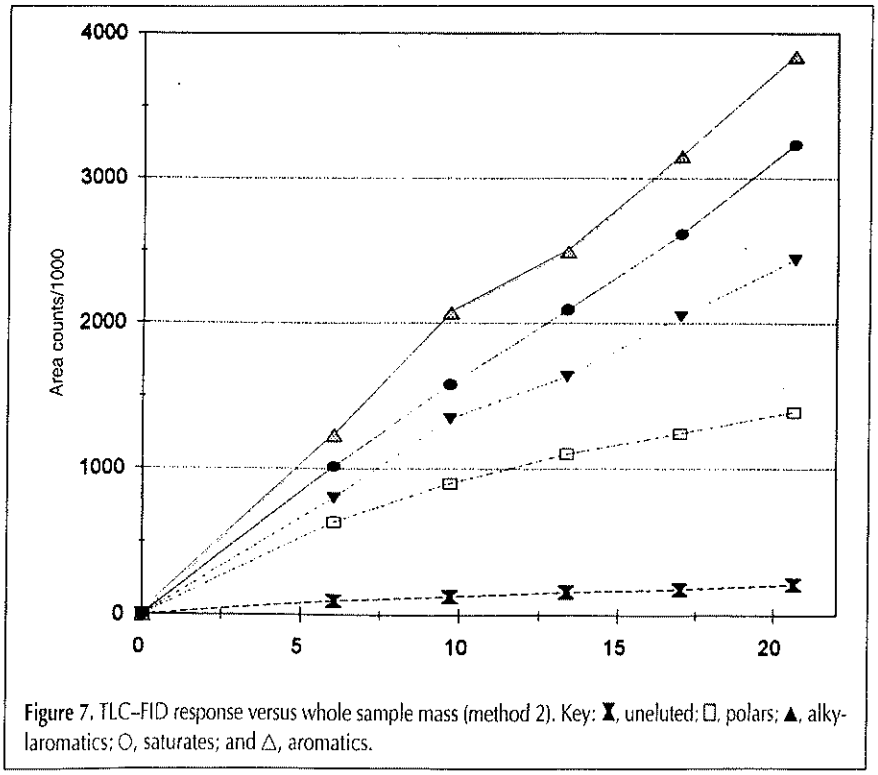

Figure 7. TLC–FID response versus whole sample mass (method 2). Key: ⧗, uneluted; □, polars; ▲, alkylaromatics; ○, saturates; and △, aromatics.

Conclusion

HGTA is important in catalytic hydroconversion in order to learn the selectivity of the different types of catalysts and to design coherent catalytic mechanisms. The selectivities of catalysts are usually compared semiquantitatively. Use of LC methods to perform quantitative comparisons implies important inconveniences.

Table VI. Method 2 Regression Coefficients

TLC–FID	0–9.712 µg	0–13.354 µg	0–16.996 µg	0–20.64 µg	% Difference*
Saturates	0.9995	0.9981	0.9975	0.9985	3.41
Alkylaromatics	0.9987	0.9896	0.9900	0.9908	8.64
Aromatics	0.9987	0.9875	0.9892	0.9925	3.74
Polars	0.9915	0.9762	0.9482	0.9248	14.39
Uneluted	0.9764	0.9539	0.9227	0.9278	10.67

* Difference between area and mass (%) in the range 15.24–20.32 µg DAO.

Table VII. Absolute Calibration (% Mass) Analysis of the Products*

Products	Saturates	Alkylaromatics	Aromatics	Polars	Uneluted
DAO	36.13	19.90	31.17	11.30	1.50
Blank run	25.78	13.26	34.78	20.07	6.11
Molybdenum naphthenate	43.99	15.60	31.93	7.03	1.45
NiMo–Al_2O_3	36.73	13.26	34.92	12.02	3.07
Plasma	39.70	12.87	33.48	12.14	1.81

* Average of 10 chromarods.

The use of the Mark 5 Iatroscan detector and the method reported here allowed for a rapid and quantitative HGTA of this kind of product without previous elimination of asphaltenes. Speed and repeatability were other positive factors versus the ASTM D2007 standard.

Because the response of this detector versus the whole sample mass was linear (approximately up to 10 µg) and passed through the origin for every chemical family studied, mass and area percentages could be used indistinctly. These results also agreed with those derived from the absolute calibration, which used LC fractions as external standards. TLC–FID has also been a successful off-line system to monitor the preparative chromatographic elution.

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