

# TLC-FID IN QUANTITATIVE HYDROCARBON GROUP TYPE ANALYSIS (HGTA) OF ASPHALTENES AND OTHER HEAVY FOSSIL FUELS

Vicente L. Cebolla, Jesús Vela, Luis Membrado, and Ana C. Ferrando

Departamento de Procesos Químicos  
Instituto de Carboquímica, CSIC  
P.O. Box 589, 50080 Zaragoza, Spain

Keywords: TLC-FID, petroleum asphaltenes and other heavy fossil fuels, TLC-scanning UV

## INTRODUCTION

Thin-Layer Chromatography with Flame Ionization Detection (TLC-FID) is mostly used in fossil fuel chemistry for quantitative hydrocarbon group type analysis (HGTA) (1-3). From an instrumental point of view, polemics about quantitative results have been reported with regard to different detector designs and sample application systems (4). Moreover, inadequate sample selection with respect to volatility properties have caused some confusing results. In order to validate TLC-FID, results should be confirmed using other techniques. On the other hand, quantitation in Chromatography is performed by previous calibration because evolution of responses of different compounds with sample load depends on each detector. Calibration becomes difficult because of the complexity of fossil fuels. Thus, the most used absolute calibration method is time-consuming, and new rapid and quantitative procedures should be developed.

In this work, instrumental performances of a modern TLC-FID system were first tested on pure *n*-alkanes and several polycyclic aromatic compounds (PACs). Detector linearity was evaluated in function of sample load and scan speed, as well as absolute response factors of the standards. Thus, criteria were developed for accurate application of TLC-FID with regard to sample volatility. Likewise, measurements of chromarod and flame temperatures permit the evaluation of whether an evaporation of compounds outside the H<sub>2</sub> flame can take place. In a second step of the research, TLC-FID results *from absolute calibration* (comparing Medium Pressure Liquid Chromatography MPLC, and other alternative methods for fraction isolation: preparative TLC and Solid Phase Extraction, SPE), and *from an alternative, fast calibration* procedure (based on a variety of the internal normalization method, VINM) were compared for different fossil fuels including asphaltenes. Repeatability and ranges for VINM application for each type of sample are reported. Finally, results from TLC-FID were validated using TLC-dual wavelength scanning UV.

## EXPERIMENTAL

**Standards and products analyzed.** Several *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs, from 3 to 6 rings), heteronuclear-PACs, and hydroxy-PACs were used as standards (Across Chimica, Belgium). The studied fossil fuels were: a heavy oil (450°C+ vacuum Brent residue); several petroleum asphaltenes: a raw one (RAsph), their derived *n*-butylated asphaltene (BuAsph) and that treated with C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub> radical (PhCH<sub>2</sub>Asph), using reductive alkylation; a coal-derived product, obtained from hydroliquefaction of a Spanish coal at 430°C for 30 min, under a N<sub>2</sub>/H<sub>2</sub> atmosphere, without solvent, and subsequently extracted with DCM.

**TLC-FID runs.** Procedure details have been reported in previous works (2, 5). Sample application (0.2-2 μL) was carried out using a 3202/IS-02 automatic sample spotter, (SES, Germany). Chromatographic separation was performed on S-III chromarods (silicagel, 5 μm particle size, 60 Å pore diameter). Quantification of peaks was carried out using an Iatron Mark 5 TLC-FID apparatus (Iatron Labs). Acquisition and treatment of data were carried out as reported elsewhere (5). Samples were solubilized in DCM (15 mg mL<sup>-1</sup>). Chromarods were developed after sample application, using two different elution sequences:

- 1) in the case of the studied heavy oil, *n*-hexane (38 min), toluene (3 min), DCM/methanol 95/5 v/v (30 sec). The following peaks were separated (± 0.01 min): saturates (retention time, r.t.: 0.18 min), aromatics (r.t.: 0.29 min), polars (r.t.: 0.39 min), and uneluted (r.t.: 0.47 min), and
- 2) in the case of the studied coal hydroliquefaction product and petroleum asphaltenes, *n*-hexane (38 min), toluene (20 min), and DCM/methanol 95/5 v/v (5 min). Peaks from sequence 2 were (± 0.01 min): saturates (r.t.: 0.14 min), aromatics (r.t.: 0.24 min), polars (r.t.: 0.36 min), and uneluted (r.t.: 0.48 min).

The amounts (μg) of the studied PACs reported throughout the text correspond to the mass effectively injected. The response of a given standard is defined as its corresponding area counts (μV s<sup>-1</sup>), *A*. The response factor of each standard is defined as *A* per mass unit, *m* (μg). Only absolute response factors are used throughout this paper.

**Flame and chromarod temperature measurements.** These were made using a data acquisition system consisting of two thermocouples (Thermocoax, type K, 0.5 mm diameter, for the flame, and Thermocoax, type S, 1 mm diameter, for the chromarods), a Fluke Hydra 2620 multichannel data

acquisition unit, and an HP-95 handheld computer to receive and store the data. A serial RS-232-C connection was used to send the data from the data acquisition unit to the computer.

**Isolation of fractions for absolute calibration.** Preparative TLC was carried out on a silicagel aluminium sheet (20 x 20 cm, 0.2 mm layer). Aromatic fraction was developed using toluene, and polar fraction using DCM/methanol 95/5, v/v. Solid Phase Extraction (SPE) was carried out on silicagel. Samples were preadsorbed in CaCO<sub>3</sub> using DCM. This solvent was further removed at 50°C under vacuum (15 mbar). The powder was placed on the top of a polypropylene syringe which contained 5 g of silicagel. Subsequently, 20 ml of toluene, and 40 ml of DCM were consecutively eluted through.

Purity of fractions were monitored using either TLC-FID or TLC-scanning UV.

**TLC-scanning UV.** Silicagel plates were also used. Eluants used for development were the same as in the case of TLC-FID. UV scanning was carried out using a Shimadzu CS9301PC densitometer, and its corresponding data acquisition and treatment software. Wavelength working range was 200-700 nm. Linear scanning in reflectance mode was used.

## RESULTS AND DISCUSSION

### TLC-FID instrumental performances with regard to quantitation

Given that one of the aims of this work was to evaluate the performance of TLC-FID technique without interferences related to the inherent volatility of the solutes, rubrene (5,6,11,12-tetraphenyl-naphthacene) was chosen to allow an in-depth study of FID linearity, apart from the above-mentioned standards. Rubrene has a high Molecular Weight (MW= 532) and low volatility (i.e., 6.373\*10<sup>-6</sup> mm Hg at 171°C). Repeatability of absolute response factors (as RSD %, which was measured at 5 µg of sample load) was, in general, lower than 5 for all the standards, regardless of their volatilities.

Linearity was evaluated with regard to sample load and scan speed (Tables 1 and 2, Figure 1). Responses of standards were adequately fitted to logarithmic regressions in the whole mass range studied (0.1-12 µg) because deviations from linearity were found at sample loads lower than 1 µg. For the lowest mass range (< 1 µg), repeatabilities were worse (11% RSD) than those obtained at higher sample loads (< 5% RSD), and this should be considered when a quantitative analysis is to be done. For sample loads higher than 1 µg, linear regressions provide adequate regression coefficients and intercepts, with low relative errors.

A particular possibility of TLC-FID is to vary the scan speed. Fitting of responses at different scan speed showed the same pattern that those previously mentioned. As scan speed decreases: i) FID response also decreases, and ii) a greater deviation from the linearity for sample loads lower than 1 µg was found. Similar response factors were obtained using 30 or 35 s scan<sup>-1</sup>. In the case of the slowest speeds (i.e., 60 s scan<sup>-1</sup>), smaller, although linear, signals were obtained. This could be used in order to inject higher sample loads in cases in which a given mass saturates the detector.

Preliminary results, obtained from the measurements of chromarod and flame temperatures seems to indicate that volatilization of rubrene prior to combustion should not take place.

Criteria about sample volatility limits for TLC-FID analysis can be developed using pure standards. Although the absolute response factors vary for different petroleum fractions (saturates, aromatics, and polars), and for different homologous series of pure compounds, they are reasonably uniform for alkanes longer than C<sub>26</sub>, and aromatics with 4 or more rings. In the case of alkanes studied, the response factor of *n*-C<sub>24</sub> (0.1 mm Hg vapor pressure at 150°C) was 0.718, and that of a saturate fraction (C<sub>32+</sub>) from a heavy oil was 0.801. *n*-Alkanes shorter than C<sub>24</sub> (vapor pressures higher than 0.3 mm Hg at 150°C) showed significantly lower response factors. In the case of PAHs, response factors were near to unity for four or more-ringed standards, and for an aromatic fraction obtained from a heavy oil.

### Calibration methods and quantitative TLC-FID results

The absolute calibration method is usually performed when a quantitative HGTA of fossil fuels is required. Thus, fractions isolated from the fossil fuel itself are used as external standards for each peak. MPLC is mostly used for fraction isolation. This is time-consuming although it is convenient when further characterization of peaks must be done using other external techniques. As well, linearity of responses for each standard is not a necessary condition for the application of this method.

A fast calibration method based on a variety of the internal normalization (VINM) was applied to several coal and petroleum products, in previous works (2, 5, 6). Its basis is as follows: if the FID response of each peak in a given sample versus the mass of whole sample can be linearized (with forced zero intercept), then this calibration procedure is theoretically equivalent to the absolute calibration. Therefore, area percentage from the chromatogram is equal to mass percentage in the problem sample within the linear zone. VINM is a quantitative, quality-control oriented procedure and no useful when preparative amounts of fractions are required. However, the tedious pre-fractionation required in the absolute calibration of fossil fuels is substituted for a rapid TLC-FID screening of several different masses of the whole sample, which can be done in 1 or 2 Iatroscan runs

(2-3 hours, and milliliters of eluants).

The agreement between both calibration methods for the studied asphaltenes is presented in Table 3. In this case, the isolation of fractions for absolute calibration was carried out using preparative TLC, instead of MPLC. Table 4 also shows an agreement between both calibration procedures for another type of sample: a coal hydroliquefaction product. Likewise, the use of either preparative TLC or SPE for absolute calibration gave similar results. These techniques save time when compared to that of MPLC (hours vs days) when absolute calibration is necessary.

#### **Quantitative application of VINM for asphaltenes and other fossil fuels**

Table 5 shows the linearity ranges from VINM in the case of the studied asphaltenes, and, for comparative purposes, in the case of a heavy oil. In this table, repeatability is expressed as a mass range semi-interval ( $\pm$  wt.%) for 95 % confidence level. A previous work (2) demonstrated that mass range semi-intervals for each peak from a heavy oil were narrower than those tolerated using the ASTM D2007. Furthermore, TLC-FID experiments are fast, and ASTM D2007 consists of a time-consuming preparative MPLC with a previous removal of asphaltenes.

Linearity from VINM is usually accomplished in restricted mass intervals, and the analyst has to choose the range of application depending on the obtained regression coefficients. Likewise, the range of sample load for application of this procedure depends on the sample nature. It must be stressed that this linearity interval refers to the whole sample and not to the mass of each fraction. Although regression coefficients are not good for the studied asphaltenes, experimental results confirmed the equivalence between the two calibration procedures.

After performing the calibration and choosing the best linearity zone for each sample according to the regression coefficients, sufficient amount of sample must be applied onto the system in order to obtain quantitative results. Sample loads must be sufficiently high for the mass of each peak (taking into account its proportion) to be greater than 1  $\mu$ g. As previously reported, masses lower than 1  $\mu$ g present RSD % of nearly 11, and deviations from the linearity.

All the studied products present ranges more than sufficient for quantitative purposes in view of the small sample loads usually spotted using this technique.

#### **Validation of TLC-FID results using an external technique (TLC-scanning UV)**

As previously mentioned, TLC-FID is limited, to some extent, by volatility considerations. Although results from absolute calibration and VINM are in accordance, this would not necessarily imply that they are the true results. For this reason, results from TLC-FID were validated in this work using HPTLC-scanning UV with absolute calibration using the corresponding fractions as external standards. These were fractionated from the products using preparative TLC. Volatility is not a limitation for quantitative application of spectroscopic techniques, such as UV.

As samples used for validation must not contain alkanes, which do not absorb in the wavelength range used, one product without alkanes was chosen for validation test. Table 4 presents the agreement between the results from TLC-FID using both absolute calibration and VINM, and from HPTLC-scanning UV.

#### **ACKNOWLEDGEMENTS**

The authors are grateful to Spanish DGICYT (Project PB93-0100) and ECSC (European Steel & Coal Community, Project 7220-EC/765) for their financial support, and also Dr. R. Bacaud (CNRS, Villeurbanne) for fruitful discussions, and Dr. R. Gruber for providing asphaltene samples.

#### **REFERENCES**

1. Selucky, M.L. *Anal. Chem.* **1983**, *55*, 141.
2. Vela, J.; Cebolla, V.L.; Membrado, L.; Andrés, J.M. *J. Chromatogr. Sci.* **1995**, *33*, 417.
3. Barman, B.N. *J. Chromatogr. Sci.* **1996**, *34*, 219.
4. Shanta, N.C. *J. Chromatogr.* **1992**, *624*, 21.
5. Cebolla, V.L.; Vela, J.; Membrado, L.; Ferrando, A.C. *Chromatographia* **1996**, *42*, 295.
6. Cebolla, V.L.; Membrado, L.; Vela, J.; Bacaud, R.; Rouleau, L. *Energy & Fuels* **1995**, *9*, 901.

**Table 1.-** Linearity of FID detector with sample load.

| Sample         | Linear Regression                     | Logarithmic regression                         |
|----------------|---------------------------------------|--|
| n-Tetracosane  | A = 663.4 * m - 19.26<br>(r = 0.9977) | Log A = 0.9363 * Log m + 2.849<br>(r = 0.9973) |
| Phenanthrene   | A = 677.5 * m - 228.7<br>(r = 0.9977) | Log A = 1.105 * Log m + 2.719<br>(r = 0.9990)  |
| Benzo-a-pyrene | A = 975.9 * m - 111.5<br>(r = 0.9986) | Log A = 1.0747 * Log m + 2.927<br>(r = 0.9973) |
| Fluorene       | A = 573.0 * m - 102.0<br>(r = 0.9934) | Log A = 1.144 * Log m + 2.629<br>(r = 0.9972)  |
| Fluoranthene   | A = 886.0 * m - 390.5<br>(r = 0.9977) | Log A = 1.148 * Log m + 2.796<br>(r = 0.9991)  |
| Pyrene         | A = 761.2 * m + 205.4<br>(r = 0.9905) | Log A = 1.0747 * Log m + 2.895<br>(r = 0.9925) |
| Rubrene        | A = 1074 * m - 53.79<br>(r = 0.9990)  | Log A = 1.084 * Log m + 2.976<br>(r = 0.9979)  |

**Table 2.-** Error percentage<sup>1</sup> of linear and logarithmic regression in the case of rubrene for different scan speeds and sample loads.

| Linear Regression                  |        |        |        |        |        |
|------------------------------------|--------|--------|--------|--------|--------|
| Scan Speed (s scan <sup>-1</sup> ) |        |        |        |        |        |
| Masa                               | 25     | 30     | 35     | 50     | 60     |
| 0.6                                | -4.69  | -11.93 | -36.94 | -61.55 | -48.67 |
| 1.8                                | 1.32   | 0.48   | -0.72  | -3.7   | -5.2   |
| 2.9                                | 0.14   | -2.95  | -4.65  | -1.54  | -7.36  |
| 4.1                                | 5.22   | 1.64   | 3.23   | -3.45  | -7.73  |
| 5.3                                | -3.59  | -0.06  | -0.32  | 3.02   | -6.54  |
| Reg. Coef <sup>2</sup>             | 0.9979 | 0.9996 | 0.9984 | 0.9974 | 0.9923 |
| Logarithmic Regression             |        |        |        |        |        |
| 0.6                                | -0.16  | -0.45  | -1.23  | -2.08  | -2.08  |
| 1.8                                | 0.16   | 0.8    | 1.88   | 2.8    | 3.07   |
| 2.9                                | -0.06  | -0.13  | 0.05   | 0.86   | 0.44   |
| 4.1                                | 0.55   | 0.1    | 0.12   | -0.81  | -1.17  |
| 5.3                                | -0.51  | -0.35  | -0.96  | -1.09  | -0.6   |
| Reg. Coef                          | 0.9993 | 0.9993 | 0.9967 | 0.9942 | 0.9946 |

<sup>1</sup> Error % between the corresponding experimental value and that predicted from the corresponding fitting curve.

<sup>2</sup> Regression coefficient obtained in the mass range 0 - 5.3 µg.

**Table 3.-** Absolute and VINM calibration of petroleum asphaltens using TLC-FID.

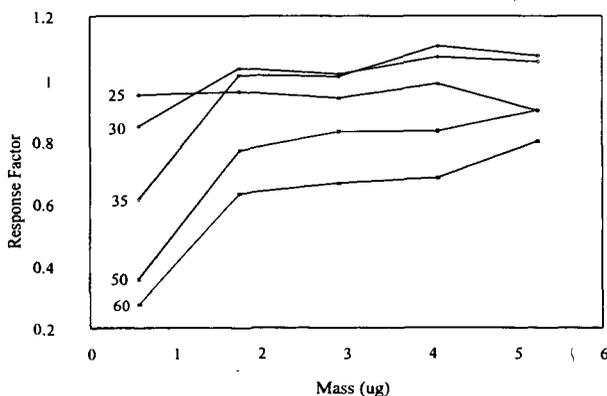
|                             | Calibration method   | Aromatics | Polars | Uneluted |
|-----------------------------|----------------------|-----------|--------|----------|
| <b>RA<sub>sph</sub></b>     | VINM                 | 1.5       | 30.7   | 67.8     |
|                             | Absolute Calibration | 1.8       | 33.8   | 64.4     |
| <b>BuAsph</b>               | VINM                 | 11.5      | 69.9   | 18.9     |
|                             | Absolute Calibration | 13.0      | 68.0   | 19.1     |
| <b>PhCH<sub>2</sub>Asph</b> | VINM                 | 23.4      | 64.7   | 11.9     |
|                             | Absolute Calibration | 20.9      | 67.1   | 12.0     |

**Table 4.-** Validation of results for a coal hydroliquefaction product.

|                      |                  | TLC-FID   |        |          |
|----------------------|------------------|-----------|--------|----------|
| Absolute calibration | Isolation method | Aromatics | Polars | Uneluted |
|                      | TLC              | 29.0      | 62.6   | 8.4      |
|                      | SPE              | 30.6      | 60.4   | 9.0      |
| VINM                 |                  | 31.2      | 60.7   | 8.1      |
|                      |                  | TLC-UVVIS |        |          |
| Absolute Calibration | Isolation method | Aromatics | Polars | Uneluted |
|                      | TLC              | 30.1      | 62.2   | 7.7      |

**Table 5.-** Linearity intervals and repeatability from VINM (TLC-FID) of the studied asphaltenes and a heavy oil.

| Sample                      | Average of Area percentage (n=5) | 95 % Confidence interval (wt%±) | Usable linearity Interval (µg)** | Regression Coefficient (r) |
|-----------------------------|----------------------------------|---------------------------------|----------------------------------|----------------------------|
| <b>RA<sub>sp</sub></b>      |                                  |                                 |                                  |                            |
| Saturates                   | ---                              | ---                             |                                  | ---                        |
| Aromatics                   | 1.5                              | 1                               | 1 - 11.2 µg                      | 0.8837                     |
| Polars                      | 30.7                             | 0.8                             |                                  | 0.9935                     |
| Uneluted                    | 67.8                             | 1.2                             |                                  | 0.9968                     |
| <b>BuAsph</b>               |                                  |                                 |                                  |                            |
| Saturates                   | ---                              | ---                             |                                  | ---                        |
| Aromatics                   | 11.5                             | 2.3                             | 1 - 14.2 µg                      | 0.9298                     |
| Polars                      | 69.9                             | 1.8                             |                                  | 0.9824                     |
| Uneluted                    | 18.9                             | 1.2                             |                                  | 0.9954                     |
| <b>PhCH<sub>2</sub>Asph</b> |                                  |                                 |                                  |                            |
| Saturates                   | ---                              | ---                             |                                  | ---                        |
| Aromatics                   | 23.4                             | 2.6                             | 1 - 9.1 µg                       | 0.9161                     |
| Polars                      | 64.7                             | 4.7                             |                                  | 0.9993                     |
| Uneluted                    | 11.9                             | 2.9                             |                                  | 0.9748                     |
| <b>Heavy Oil</b>            |                                  |                                 |                                  |                            |
| Saturates                   | 33.2                             | 0.63                            |                                  | 0.9994                     |
| Aromatics                   | 57.4                             | 0.74                            | 1 - 20.6 µg                      | 0.9931                     |
| Polars                      | 12.9                             | 0.19                            |                                  | 0.9758                     |
| Uneluted                    | 0.5                              | 0.09                            |                                  | 0.9697                     |



**Figure 1.-**Response factors (A/m) in the case of rubrene for different scan speeds and sample loads.