

Suitability of Thin-Layer Chromatography–Flame Ionization Detection with Regard to Quantitative Characterization of Different Fossil Fuel Products. II. Calibration Methods Concerning Quantitative Hydrocarbon-Group Type Analysis

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Abstract

Time-consuming external standard-based calibration methods are usually performed for hydrocarbon group type analysis (HGTA) of fossil fuels, regardless of the instrumental chromatographic technique. In this work, HGTA of a broad variety of coal and petroleum products is performed using a modern thin-layer chromatography–flame ionization detection (TLC–FID) system and a rapid method based on internal normalization. Repeatability, linear intervals, and sample load ranges for quantitative application of this method are detailed for different products that cover a broad range of boiling points and chemical functionalities in the field of fossil fuels: a heavy oil and its derived hydrocracked products, raw and chemically-modified petroleum asphaltenes, a coal-tar pitch, several coal extracts, and coal hydroliquefaction products. Results from external standard calibration and a normalization method (both obtained by TLC–FID) are in agreement, and they are validated using TLC–ultraviolet scanning. The use of the latter demonstrates that TLC–FID can also be applied to products such as coal extracts and hydroliquefaction products, despite these products being more volatile than petroleum asphaltenes or heavy oils. For preparative purposes when external calibration is necessary, preparative TLC and SPE are less time-consuming alternatives to MPLC fractionation, providing similar results.

Introduction

Quantitative analysis using instrumental chromatography usually involves a prior calibration step. The responses of each

separated compound for a given detector show a particular dependence on chemical structure and may also change with sample load. In the case of mixtures of pure compounds which are known and available, calibration is easily carried out using different methods. However, when mixtures are composed of unavailable or unknown compounds (i.e., many PAC-related environmental samples), calibration becomes more difficult.

Thin-layer chromatography (TLC) with flame ionization detection (FID) has been used for hydrocarbon-group type analysis (HGTA) of fossil fuel samples (1–4). HGTA separates each fossil fuel sample into several compound classes (i.e., saturates, aromatics, polars, and uneluted fractions). TLC–FID is used in some cases as an instrumental technique to perform HGTA without previous calibration, with good results. However, this possibility can not be considered for general application, because there are many cases for TLC–FID in which there is need for prior calibration.

Even in the case of HGTA of fossil fuel samples, where each peak is a mixture of compounds and their response cannot be assumed to be constant, a calibration step seems necessary and is usually performed by means of the use of external standards. Sample fractions derived from the fossil fuel and isolated using a preparative method are the most suitable and common calibration standards. This procedure, usually referred to as “absolute calibration”, is too slow to be carried out on a regular basis. In fact, because it involves the actual separation of the fractions to be analyzed later, it even makes the TLC–FID analysis redundant; if performed on each sample, as it should be, the quantitative analysis will be known in advance as a result of the preparative method. Therefore, even when the absolute calibration is carried out, a similar response for the peaks of a set of samples is assumed, and it is only performed on one of them. This makes the absolute calibration practical, but again introduces risky assumptions for the quantitation procedure.

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A different scheme seems to be needed. The ideal procedure should control the differences in the nature of each sample but be fast enough to be performed on each of them. An internal calibration method seems the only alternative. Absolute calibration could be used in this case to validate the general suitability of the internal method but not as a necessary step for the analysis of each sample.

In any case, absolute calibration remains the only dependable method of reference. In this work, we have focused on the study of the conditions that justify (or do not justify) the need for a calibration step in HGTA and the application of a previously developed internal calibration method that suits the needs for a fast HGTA of a broad set of fossil fuel samples. The results have been validated using new absolute calibration procedures faster than those usually reported. The results have been contrasted with a different instrumental chromatographic technique: TLC-ultra-violet scanning (TLC-UV).

Experimental

Products analyzed

Deasphalted petroleum heavy oil

Deasphalted petroleum heavy oil (DHO) is a deasphalted oil from a 450°C+ vacuum Brent residue (5).

Hydrocracking products

Hydrocracking products derived from DHO were obtained after DHO hydroconversion (440°C, 1 h, 14 MPa H₂ pressure) without catalyst (blank) or using different catalysts: molybdenum naphthenate (MoNaph), Ni-Mo-Al₂O₃ (NiMo), plasma Ni solid (plasma). Details were published elsewhere (5).

Petroleum asphaltenes

A raw petroleum asphaltene (RAsph), its *n*-butylated-derived asphaltene (BuAsph), and its benzyl-derived asphaltene (PhCH₂Asph) were also analyzed. Chemical modification was carried out according to the experimental conditions reported by Miyake et al. (6).

Coal-tar pitch

A high-temperature coal-tar pitch (CTP) was analyzed, the properties of which have already been reported elsewhere (7).

Coal extracts

Several coal extracts with dichloromethane (DCM) obtained from different Spanish coals using a Soxtec (Tecator, Sweden) model HT-2 apparatus were studied (8): Utrillas lignite (DCM-UL), Mequinenza lignite (DCM-ML), Puertollano bituminous coal (DCM-PB), and Pozo Pilar sub-bituminous coal (DCM-PP).

Coal hydroliquefaction products

Several hydroliquefaction products (9) were

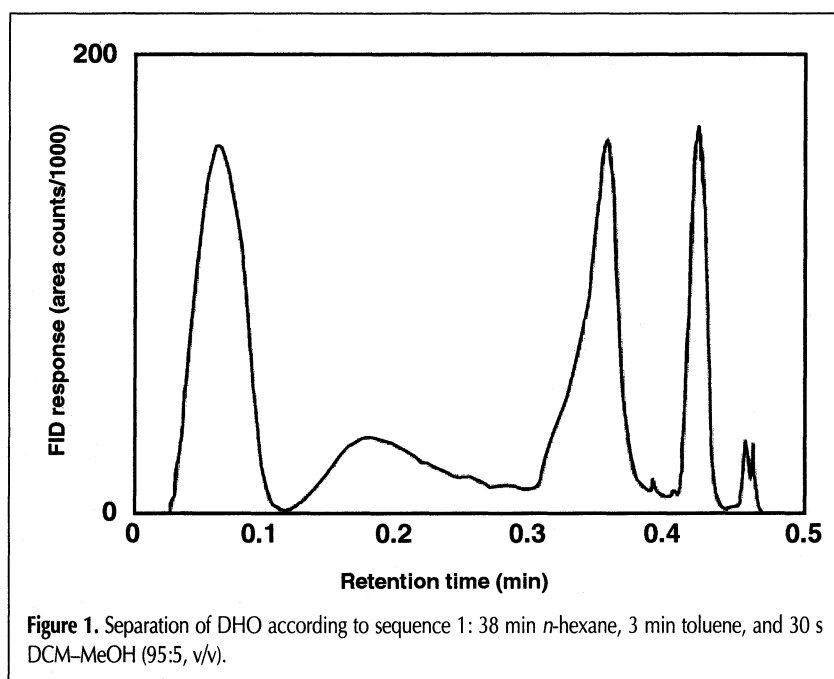
selected in order to cover a wide range of hydroliquefaction conditions: hydroliquefaction of Utrillas lignite (HUL) at 375°C for 30 min under an N₂-H₂ atmosphere (total pressure, 7 MPa; partial pressure of H₂, 1.4 MPa) without solvent and subsequent extraction with tetrahydrofuran (THF); hydroliquefaction of Mequinenza lignite (HML) at 415°C for 30 min under an N₂-H₂ atmosphere (total pressure, 10 MPa; partial pressure of H₂, 7 MPa) without solvent and subsequent extraction with DCM; hydroliquefaction of Puertollano coal (HPB) at 400°C for 30 min under an N₂-H₂ atmosphere (total pressure, 10 MPa; partial pressure of H₂, 7 MPa) with cyclohexane as liquefaction solvent (solvent-coal [5:1, w/w]) and subsequent extraction with DCM; hydroliquefaction of Pozo Pilar coal (HPP) at 430°C for 30 min under an N₂-H₂ atmosphere (total pressure, 10 MPa; partial pressure of H₂, 5 MPa) without solvent and subsequent extraction with DCM.

TLC-FID experiments

Sample application (5–30 µg) was carried out using a 3202/IS-02 automatic sample spotter (SES, Schaidt, Germany). Chromatographic separation was performed on S-III chromarods (silica gel, 5-µm particle size, 60-Å pore diameter). Quantitation of peaks was carried out using an Iatroscan Mark 5 TLC-FID apparatus (Iatron Labs, Tokyo, Japan). Procedure details have been reported in previous works (3,7). FID scanning was performed at 30 s/scan using 160 mL/min H₂ flow and 2100 mL/min air flow.

Samples were dissolved in DCM (15 mg/mL). Chromarods were developed after sample application using two different elution sequences: one for DHO (*n*-hexane, 38 min; toluene, 3 min; DCM-methanol [95:5, v/v], 30 s) and one for the other products (*n*-hexane, 38 min; toluene, 20 min; and DCM-methanol [95:5, v/v], 5 min).

Sequence 1 separated (± 0.01 min) saturates (retention time 0.18 min), aromatics (retention time 0.29 min), polars (retention time 0.39 min), and uneluted components (retention time 0.47 min) (Figure 1). Sequence 2 separated (± 0.01 min) saturates



(retention time 0.14 min), aromatics (retention time 0.24 min), polars (retention time 0.36 min), and residue (retention time 0.48 min) (Figure 2). The products analyzed using Sequence 2 either did not contain saturates or the saturates were present in very low proportions (lower than 3%).

Isolation of fractions from fossil fuels for calibration purposes

Medium-pressure liquid chromatography

Medium-pressure liquid chromatography (MPLC) on silica gel was used to obtain fractions from DHO. Details about the chromatographic isolation have been reported elsewhere (3).

Preparative TLC

Two fractions (aromatic and polar) were obtained from HPP using TLC on a silica gel aluminium sheet (0.2-mm layer, Panreac, Barcelona, Spain). Aromatic fractions were developed using toluene, and polar fractions were developed using DCM-

methanol (95:5, v/v). The separated zones were dissolved using DCM filtered on a teflon membrane (cameo-13F, 0.45- μ m pore size, Scharlau, Barcelona, Spain), and the solvent was removed at 50°C under a vacuum (15 mbar).

Solid-phase extraction

Solid-phase extraction (SPE) of HPP was carried out on silica gel (70–230 mesh ASTM, Merck, Darmstadt, Germany). First, 200 mg of sample was preadsorbed in CaCO₃ using DCM. This solvent was further removed at 50°C under a vacuum (15 mbar). The powder was placed on the top of a polypropylene syringe which contained 5 g of silica gel. Subsequently, 20 mL of toluene and 40 mL of DCM were consecutively eluted. Fractions were collected every 2.5 mL. After this, eluants were removed as previously cited.

The purity of the fractions isolated using the described techniques was monitored using TLC-FID, TLC with dual wavelength scanning densitometry (model CS9301PC, Shimadzu, Kyoto, Japan), or both techniques.

TLC-UV experiments for verification of TLC-FID results

Sample application was carried out using the aforementioned autospotter with the same mass range. Eluants used for development were the same as in the case of TLC-FID, although development times were slightly different (12 min with toluene and 4 min with DCM-MeOH). UV scanning was carried out using a Shimadzu CS9301PC densitometer and its corresponding data acquisition and treatment software. The wavelength working range was 200–700 nm. Linear scanning in reflectance mode was used. The beam size was 0.4 × 0.4 mm. Data output was linearized using the Kubelka-Munk procedure.

Results and Discussion

Repeatability of TLC-FID experiments

Repeatability of TLC-FID analysis must be one of the first concerns if a quantitative analytical procedure is to be developed. Therefore, repeatability was studied and compared with the values from a standard gravimetric HGTA, ASTM D2007.

The relative standard deviation (%RSD) of area percentages were used as comparative values, and they were calculated for each product studied (Tables I–III) and the mass range semi-interval (\pm weight percent) for a 95% confidence level. %RSD is defined as

$$\%RSD = \sigma \times 100 / \mu \quad \text{Eq 1}$$

where σ is the sample standard deviation and μ is the average of area counts. In this case, five measurements were used for the calculation of σ and μ .

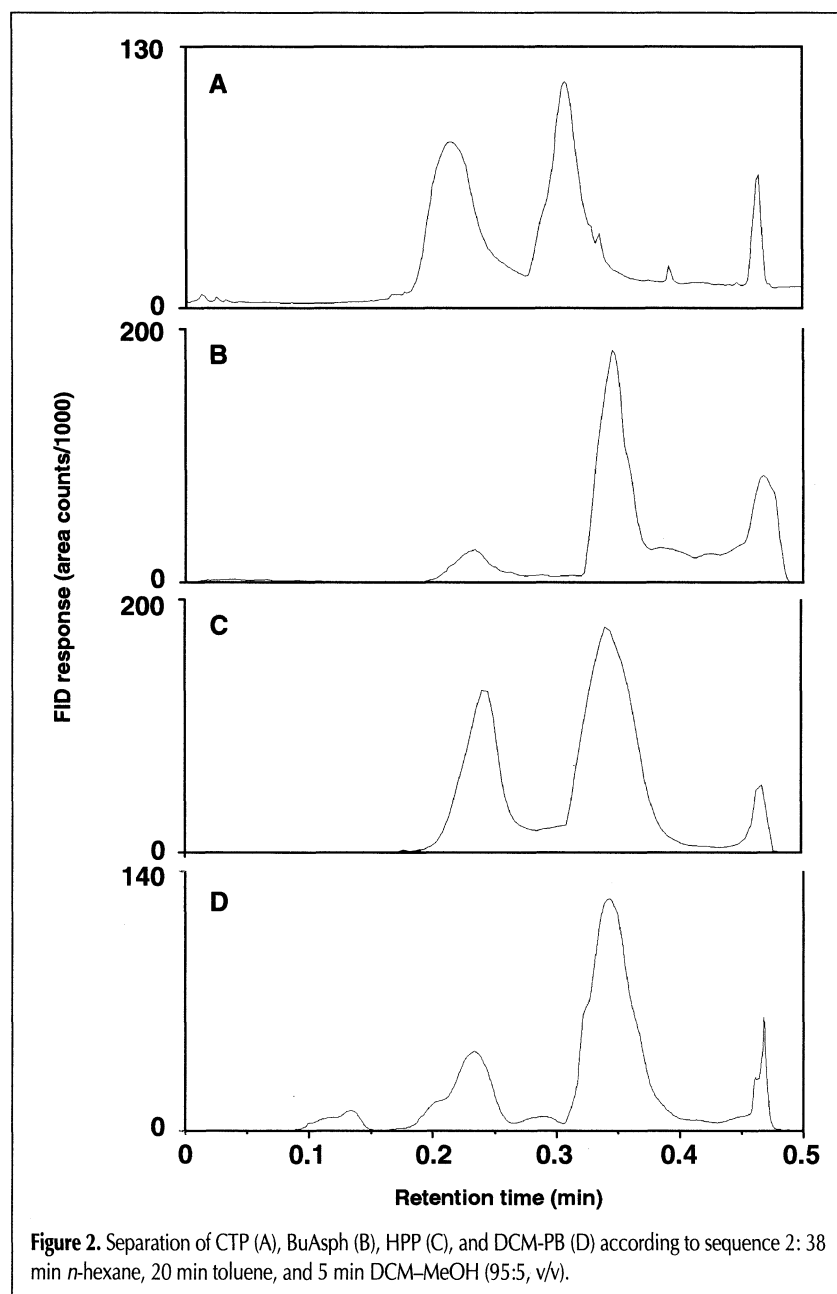


Table I. Quantitative Results of Coal Extracts and CTP Using VINM

Sample	Average of area percentage (<i>n</i> = 5)	95% Confidence interval (weight %, \pm)	%RSD	Usable linearity interval (μg)	Regression coefficient
CTP					
Saturates	–	–	–		–
Aromatics	52.8	1	1.06	1–20.0 μg	0.9977
Polars	39.0	0.73	1.85		0.9983
Uneluted	9.4	0.68	3.51		0.9950
DCM-UL					
Saturates	9.6	0.31	2.57		0.9915
Aromatics	7.6	0.78	8.37	1–18.5 μg	0.9934
Polars	48.1	1.49	2.47		0.9944
Uneluted	34.1	2.18	5.15		0.9944
DCM-ML					
Saturates	1.0	0.17	14.09		0.9612
Aromatics	1.0	0.11	11.21	1–19.4 μg	0.9761
Polars	93.8	0.53	0.46		0.9935
Uneluted	4.2	0.29	5.39		0.9922
DCM-PB					
Saturates	5.6	0.42	6.01		0.9938
Aromatics	22.6	0.5	1.75	1–11.7 μg	0.9973
Polars	63.6	2	2.52		0.9955
Uneluted	8.2	1.96	19.46		0.9935
DCM-PP					
Saturates	7.3	1.24	8.72		0.9910
Aromatics	3.2	0.74	12.85	0–15.7 μg	0.9742
Polars	84.7	1.61	1.54		0.9969
Uneluted	4.8	1.2	19.96		0.9219

Table II. Quantitative Results of Coal-Hydroliquefaction Products Using VINM

Sample	Average of area percentage (<i>n</i> = 5)	95% Confidence interval (weight %, \pm)	%RSD	Usable linearity interval (μg)	Regression coefficient
HML					
Saturates	1.3	0.1	8.69		0.9680
Aromatics	24.9	1.5	4.68	1–30.8 μg	0.9895
Polars	61.8	1.6	2.07		0.9995
Uneluted	11.7	0.6	4.23		0.9961
HPB					
Saturates	0.7	0	3.22		0.9939
Aromatics	13.6	0.8	5.1	1–27.9 μg	0.9933
Polars	76.9	1.1	0.74		0.9992
Uneluted	8.7	0.9	7.27		0.9900
HPP					
Saturates	–	–	–		–
Aromatics	30.9	2.2	5.9	1–35.0 μg	0.9984
Polars	62.4	1.5	1.86		0.9921
Uneluted	6.7	0.9	10.23		0.9925
HUL					
Saturates	–	–	–		–
Aromatics	13.2	0.53	3.26	1–20.59 μg	0.9961
Polars	74.6	0.55	0.59		0.9930
Uneluted	12.2	0.19	1.22		0.9592

Tables I–III show the results concerning the repeatability of TLC–FID experiments for different fossil fuel products. A typical fossil fuel chromatogram presents three or four peaks which correspond to their respective compound-class fractionation (also called HGTA or SARA). Repeatability results are given in Tables I–III for each peak. Repeatability results are not frequently referred to in the literature with regard to the analysis of coal products, mainly because the current methods for compound-class characterization are based on preparative LC. Thus, the duration of the fractionations precludes the adequate repetition of experiments, and repeatability may not be good because of the many steps required for analysis.

Those peaks which are small (regardless of sample nature) in Tables I–III present high values of %RSD of area percentages. This is obviously due to low values of the averages of area percentages (μ) and not due to high values of σ .

When repeatability results are expressed as mass range semi-intervals for a given confidence level (95%), repeatabilities can be considered clearly satisfactory. Therefore, mass range semi-

intervals obtained using TLC–FID for the products studied are, in general, lower than ± 2 weight percent. In the case of DHO, mass range semi-intervals for each peak were reported in a previous work to be narrower than those tolerated using ASTM D2007. Another advantage over ASTM D2007 is that TLC–FID experiments are fast, whereas ASTM D2007 consists of time-consuming preparative MPLC which requires a prior removal of asphaltene (10). Furthermore, it should be pointed out that, in this work, TLC–FID was applied directly to asphaltene with adequate repeatabilities.

Calibration methods and quantitative TLC–FID results

HGTA of fossil fuel samples is sometimes performed without any calibration step (4), and in some cases, very peculiar calibration procedures are used instead (11,12). The main question concerning the need for a calibration step pertains to the influence of the nature of the sample on the TLC–FID results.

When the samples to be analyzed are of a very similar chemical nature and sufficiently high molecular size (e.g., lubricants),

Table III. Quantitative Results of Petroleum Asphaltene and DHO Using VINM

Sample	Average of area percentage ($n = 5$)	95% Confidence interval (weight %, \pm)	%RSD	Usable linearity interval (μg)	Regression coefficient
RAsh					
Saturates	–	–	–		–
Aromatics	1.5	1	41.6	1–11.2 μg	0.8837
Polars	30.7	0.8	1.3		0.9935
Uneluted	67.8	1.2	1.3		0.9968
BuAsph					
Saturates	–	–	–		–
Aromatics	11.5	2.3	12.9	1–14.2 μg	0.9298
Polars	69.9	1.8	1.7		0.9824
Uneluted	18.9	1.2	4.3		0.9954
PhCH ₂ Asph					
Saturates	–	–	–		–
Aromatics	23.4	2.6	7.2	1–9.1 μg	0.9161
Polars	64.7	4.7	4.7		0.9993
Uneluted	11.9	2.9	11.2		0.9748
DHO					
Saturates	33.2	0.63	1.54		0.9994
Aromatics	57.4	0.74	1.12	1–20.6 μg	0.9931
Polars	12.9	0.19	1.24		0.9758
Uneluted	0.5	0.09	14.0		0.9697

Table IV. Validation of Results for HPP

Isolation method		Aromatics	Polars	Uneluted
TLC–FID				
Absolute calibration	TLC	29.0	62.6	8.4
	SPE	30.6	60.4	9.0
VINM		31.2	60.7	8.1
TLC–UV/VIS				
Absolute calibration	TLC	30.1	62.2	7.7

most or all of the effects that change the response of TLC-FID that were studied in the previous paper (13) can be ignored. This is the case for samples analyzed by Barman (4), and for this particular case or similar cases, area percentages can be directly used as mass percentages. It is reasonable to assume that all peaks for these samples have the same type of behavior toward TLC-FID.

When the samples to be analyzed show an appreciable range of variation in chemical nature or molecular size (e.g., oils) (3,11,12), the previous hypothesis is no longer acceptable, but the limited range of variation can be used to reduce the number of reference products used. A synthetic reference product can be easily produced by mixing all of the samples, and a calibration carried out using this synthetic product minimizes the deviations for the other samples. Bharati et al. (11,12) described situ-

ations where a mixture of all the study samples was used as the only reference product, which allowed the calculation of area-mass coefficients that were applied unchanged to all samples in the variation range.

In any case, both procedures are acceptable for samples of a particular nature but are not general enough to be applied to an unknown general fossil fuel sample. Alternatively, a fast calibration method based on a variety of the internal normalization procedure (VINM) allows for a fast calibration in a wider range of samples and gives a simple criterion to characterize the amount of deviation from the ideal quantitative conditions.

VINM was applied to several coal and petroleum products (CTP and DHO), in previous works (3,9). Its basis is as follows: if the FID response of each peak in a given sample versus the mass of the whole sample can be linearized (with forced zero intercept),

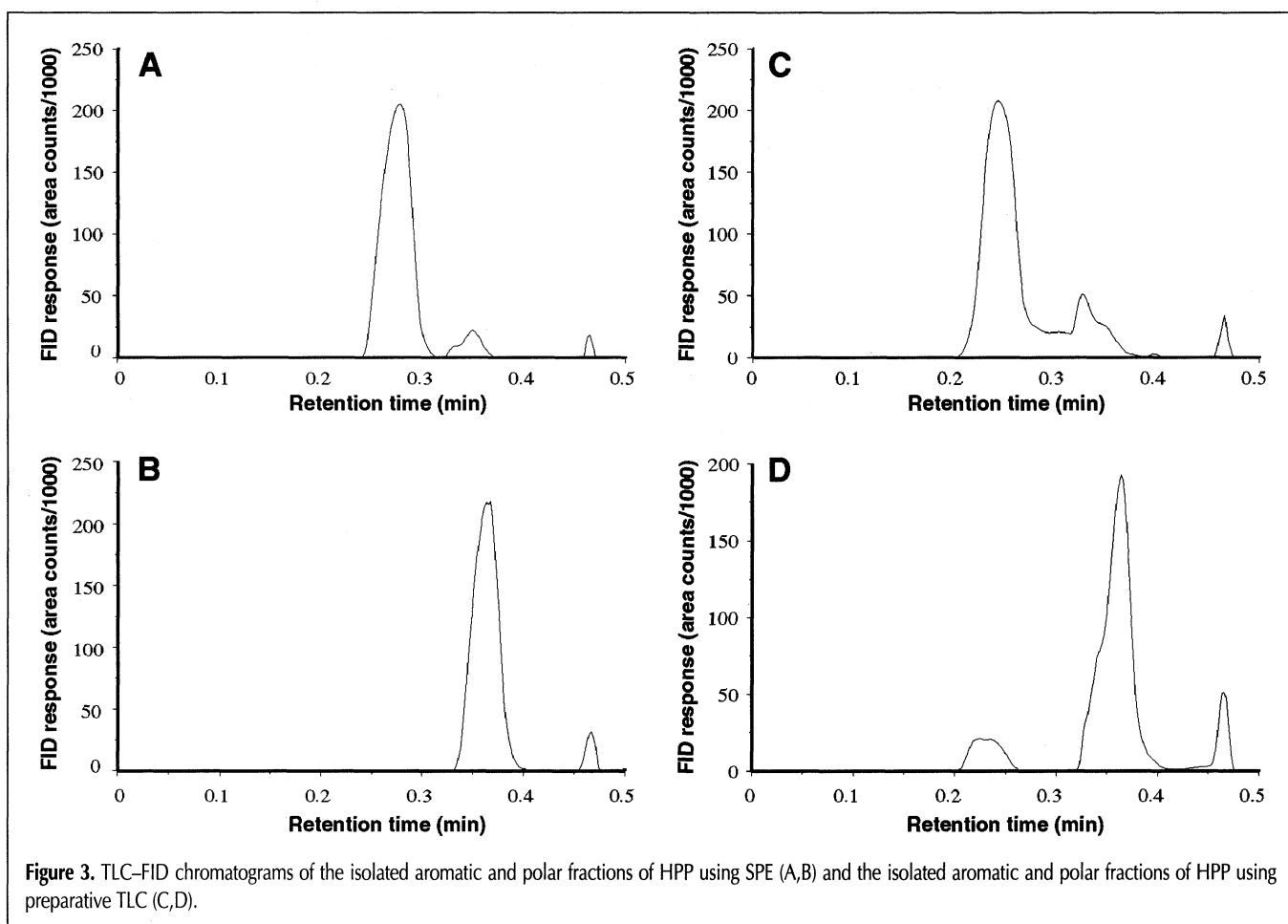


Figure 3. TLC-FID chromatograms of the isolated aromatic and polar fractions of HPP using SPE (A,B) and the isolated aromatic and polar fractions of HPP using preparative TLC (C,D).

Table V. Absolute and VINM Calibration of Petroleum Asphaltenes Using TLC-FID

	Calibration method	Aromatics	Polars	Uneluted
RAsph	VINM	1.5	30.7	67.8
	Absolute calibration	1.8	33.8	64.4
BuAsph	VINM	11.5	69.9	18.9
	Absolute calibration	13.0	68.0	19.1
PhCH ₂ Asph	VINM	23.4	64.7	11.9
	Absolute calibration	20.9	67.1	12.0

then this calibration procedure is theoretically equivalent to the absolute calibration. Therefore, the area percentage from the chromatogram is equal to the mass percentage in the problem sample within the linear zone. VINM is a quantitative, quality-control-oriented procedure and is not useful when preparative amounts of fractions are required. However, the tedious pre-fractionation required in the absolute calibration of fossil fuels is substituted with a rapid TLC-FID screening of several different masses of the whole sample and can be done in one or two Iatroscan runs (2–3 h, milliliters of eluants).

The agreement between both calibration methods was experimentally confirmed on DHO in a previous work (3). Confirmation for a very different product, HPP, is presented in Table IV.

With regard to the absolute calibration, one of the aims of this work was to study alternative techniques to MPLC in order to shorten the time of fractionation. Obviously, the final result of the analyses should be similar. Table IV shows results corresponding to the absolute calibration of HPP using either preparative TLC or SPE as fractionating techniques, as well as those corresponding to the application of VINM.

The use of either preparative TLC or SPE for absolute calibration provided similar results between them and was similar to VINM results. Figure 3 shows TLC-FID chromatograms of the isolated aromatic and polar fractions of HPP using SPE and preparative TLC. This illustrates that an adequate isolation was carried out by these techniques. SPE and TLC save time with regard to MPLC (hours versus days) for absolute calibration purposes. In short, VINM is a faster calibration procedure.

Quantitative application of VINM for coal and petroleum products

Obviously, linearity with VINM is usually accomplished in restricted mass intervals, and the analyst has to choose the range of application based on the regression coefficients obtained. Likewise, the range of sample load for the 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. Sample load ranges for different coal and petroleum products are presented in Tables I–III.

After performing the calibration and choosing the best linearity zone for each sample according to the regression coefficients, a sufficient amount of sample must be applied to 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 µg. As previously reported (13), masses lower than 1 µg present a %RSD of nearly 11 and deviations from the linearity. All of the studied products present ranges more than sufficient for quantitative purposes (in view of the small sample loads usually spotted with this technique).

The studied asphaltene illustrate the relativity of the values for regression coefficients that can be considered acceptable. In the case of RAsph, the aromatic peak shows a regression coefficient of 0.8837 associated with average area values of 1.5%. In absolute terms, the regression coefficient is not high enough, but it belongs to a peak of low abundance. Therefore, the error caused by an inaccurate determination of the mass content in aromatics for the complete analysis of the sample is not relevant.

BuAsph and PhCH₂Asph show regression coefficients for the

aromatic peak a little higher than the one observed for RAsph, and they are associated with more important percentages in area. In any case, they are not the most abundant peak. The errors associated with the calculation of their mass percentages should have a higher influence on the error of the complete analysis, but their value (because of their better regression coefficients) should be smaller in absolute terms. The final result is in general agreement with the values derived from absolute calibration (Table V).

In summary, because the VINM method provides a sample mass range for the whole sample, the better regression coefficients will be found for the most abundant peaks, and the error in mass percentage will be minimal for them but will increase for less abundant peaks that could even fall into mass ranges (below 1 µg) that do not show a good repeatability (13).

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

It has previously been reported that results from TLC-FID must be taken with caution for samples with volatilities higher than those corresponding to alkanes shorter than C₂₄ and aromatics with 3 rings or less (13). Furthermore, controversy concerning the evaporation of some samples outside the flame for TLC-FID has been reported (14). 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 TLC-UV with absolute calibration using the corresponding standards. These were fractionated from the products using preparative TLC as previously mentioned, and subsequent absolute calibration was done. Volatility is not a limitation for the quantitative application of UV scanning.

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

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