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High-performance liquid chromatography coupled off-line with capillary gas chromatography Application to the determination of the aromatics content in middle distillates

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Abstract

The off-line coupling of normal-phase HPLC and capillary GC was used to determine the total aromatics content of middle distillates. Samples doped with internal standards were injected into the liquid chromatograph and the two collected fractions, saturates and aromatics, were further analysed by capillary GC. Good repeatability of the analysis was obtained for this determination on both gas oils and kerosenes and there was good agreement with other analytical methods (mass spectrometry and preparative liquid chromatography).

1. Introduction

The precise determination of the aromatics content of middle distillates (gas oils and kerosenes) is of major concern for prosses engineers. The group-type separation of hydrocarbons by liquid chromatography has been widely reported [1–3]. An HPLC method has also recently been normalized (European Committee for Standardization: ECS) that gives mono-, di- and polyaromatics contents in commercial gas oils with fairly good repeatability and reproducibility for individual and total aromatics. However, it has been stressed that this method is sample sensitive, particularly for mildly hydrotreated gas oils. This hinders the usefulness of the method for the design of hydrotreatment processes [4]. Mass spectrometry, on the other hand, needs further adaptation of the data treatment matrix to deal with kerosenes cuts.

The coupling of a gas chromatograph to a liquid chromatograph is a powerful tool for achieving a high separation efficiency and adapting a quasi-universal detector to HPLC. However, for the application in question, the choice between on-line and off-line coupling must be made. The techniques for transferring a large volume of liquid into a gas chromatograph have been extensively described [5]. The application of on-line coupling to petroleum products analysis has also been described, mainly for the identification of polycyclic aromatic compounds [6,7]. For on-line coupling, two types of interface must be considered: either a "loop-type" or an

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"on-column" interface. On the one hand, the "loop-type" interface is known to produce losses of the more volatile compounds of the sample and therefore seems unsuitable for the analysis of gas oils whose initial cut point can start at 150°C. On the other hand, the "on-column" interface is not suitable for the injection of the large volumes of liquid obtained with standard HPLC columns. For these reasons, off-line coupling was chosen.

The aim of this study was to evaluate the off-line coupling of HPLC with GC to obtain an analytical "reference" method for this type of sample taking advantage of the universal response of flame ionization detection (FID).

2. Experimental

2.1. Materials

The eluent for HPLC and semi-preparative liquid chromatography were HPLC-grade *n*-pentane and HPLC-grade dichloromethane and methanol, respectively (Solvants, Documentation, Synthèses, Peypin, France), degassed with helium. As standards, triacontane (n-C_{30}) (>99%) was obtained from Aldrich (St. Quentin Fallavier, France) and *n*-ocatane (n-C_8) and *o*-xylene (both >99%) from Merck (Darmstadt, Germany).

Silica gel, 75–100 μm (100–200 mesh) (Davison Chemical, USA) and alumina gel, 60–230 μm (alumina 90, 70–230 mesh; Merck) were used as stationary phases for semi-preparative liquid chromatography.

2.2. Instruments and columns

The semi-preparative liquid chromatographic equipment consisted of an injection pump capable of delivering the eluent at a flow-rate of 2 ml/min (Model 420 pump; Kontron, Zurich, Switzerland), a calibrated injection loop of 4 ml and a stainless-steel column [110 cm × 9.53 mm (3/8 in.) O.D.]. The column was dry-filled with a bottom bed of silica (ca. 25 g) and completed with an upper bed of alumina, both activated overnight at 180°C in an oven.

The HPLC equipment consisted of a Waters (Milford, MA, USA) 600-MS solvent-delivery system equipped with a back-flush valve (Waters automated switching valve) and a UV detector (Spectromonitor 4100; LDC, Riviera Beach, FL, USA). The columns were either two aminosilica columns (as in the ECS method) or two silica columns, both obtained from Applied BioSystems (San Jose, CA, USA). These columns were 250 mm × 6.35 mm (1/4 in.) O.D. and showed a resolution for the separation of cyclohexane–*o*-xylene of 5 and 13.9, respectively, measured with one column.

The capillary GC equipment consisted of a Model 3500 gas chromatograph (Varian, Sunnyvale, CA, USA) equipped with an on-column injector and an autosampler (Varian 8035). The fused-silica capillary column was coated with a DB-1 methylsilicone stationary phase with a film thickness of 0.25 μm (60 m × 334 μm I.D.) (J&W Scientific, Rancho Cordova, CA, USA). The data acquisition and processing were performed with an HP1000 system (Hewlett-Packard, Avondale, PA, USA).

The mass spectrometer was a Kratos (Manchester, UK) MS50. The data were analysed using a modified Fitzgerald method according to ref. [8].

2.3. Procedure

For semi-preparative liquid chromatography, the eluents used were *n*-hexane for the elution of the saturates fraction and dichloromethane–methanol (9:1 v/v) for the elution of the aromatics fraction. About 2.5 g of sample, precisely weighed, were dissolved in 10 ml of *n*-hexane. The collection of the fractions was carried out on a fixed elution time basis as the method had been previously validated on a wide range of samples using refractive index (RI) and UV detectors. The solvents were carefully evaporated at room temperature under a nitrogen flow and a mass balance was made. The same type of separation using different eluents has also been described elsewhere [9].

For HPLC separation with aminosilica columns, the mobile phase (*n*-pentane) was used without further treatment. For separations with the silica columns, a set of two precolumns was installed between the pump and the injection valve in order to minimize the water content of pentane. One of the columns was filled with molecular sieve 4 Å and the other with silica activated at 180°C overnight. The eluent flow-rate was set at 1 ml/min. The samples, gas oil or kerosene, were diluted in *n*-pentane at about 20% (w/w) with addition of internal standards: *n*-C_8, *n*-C_{30} and *o*-xylene. The volume injected was 20 μl. A back-flush was applied to elute the aromatics as a single peak.

As long-chain aliphatic hydrocarbons elute close to the aromatics and long-chain substituted alkylaromatic hydrocarbons elute close to the saturates, an RI and a UV detector were used to monitor the separation. Typical chromatograms of a gas oil obtained with these detectors are shown in Fig. 1. The RI detector was first used to monitor the separation of aromatic from aliphatic compounds because both show a response on the RI detector (Fig. 1a). The UV detector was used at a wavelength of 210 nm to determine the back-flush point (Fig. 1b). The saturates fraction was collected between the retention time t_0 determined with RI detection and the back-flush time determined with UV detection; the aromatics fraction was collected with the help of the UV detector at 210 nm. Fractions of 2–4 ml were collected with concentrations of about 2000 ppm of saturates and 500 ppm of aromatics.

Further, for some analyses with correct back-flush times, the absence of monoaromatics in the collected saturates fraction was checked using UV analysis at 200 nm, a wavelength that enhances the monoaromatics response.

For capillary GC analysis, the carrier gas was helium at a pressure of 2.07 MPa (30 p.s.i.), the FID sensitivity was set to 10^{-12} A and the injection volume was 1 μl. The injector temperature was programmed from 40 to 300°C at 150°C/min and the temperature programme for elution was from 40 to 320°C at 3°C/min.

Sequences of injections including pentane injections (blank) were carried out and the integration of chromatograms was performed after subtraction of the blank. The total aromatics content was either calculated from the difference between 100% and the percentage of the saturates fraction using both internal standards (*n*-C_8 and *n*-C_{30}) or from the aromatics fraction using the *o*-xylene standard. It was observed that a repeatable and accurate determination of the saturates and aromatics contents of the fractions needs a minimum concentration level of product in the injected fraction and careful washing of the automated sampler fitted to the gas chromatograph.

3. Results and discussion

3.1. Gas oil analysis

The first step in this study was to optimize the experimental conditions. The method was evaluated with the two types of HPLC stationary phases using a well characterized gas oil (CEN17) containing about 27% (w/w) of aromatics.

It was shown that the aminosilica column requires particular attention to the back-flush time applied. However, the silica column gives a greater latitude for the choice of back-flush time owing to its much better resolution between saturates and aromatics.

Multiple samples of HPLC fractions were obtained and analysed by GC. Fig. 2 shows an example of a gas chromatogram of each fraction. The determination of the aromatics content was systematically observed to depend on the procedure used: the aromatics percentage obtained from the saturates fraction quantified using *n*-C_8 was greater than that obtained from the aromatics fraction quantified using *o*-xylene, which was in turn greater than that obtained from the saturates fraction quantified using *n*-C_{30}. Determination using the *n*-C_{30} internal standard was found to be unsuitable mainly owing to peak tailing. The determination using *n*-C_8 was considered to overestimate the aromatic content

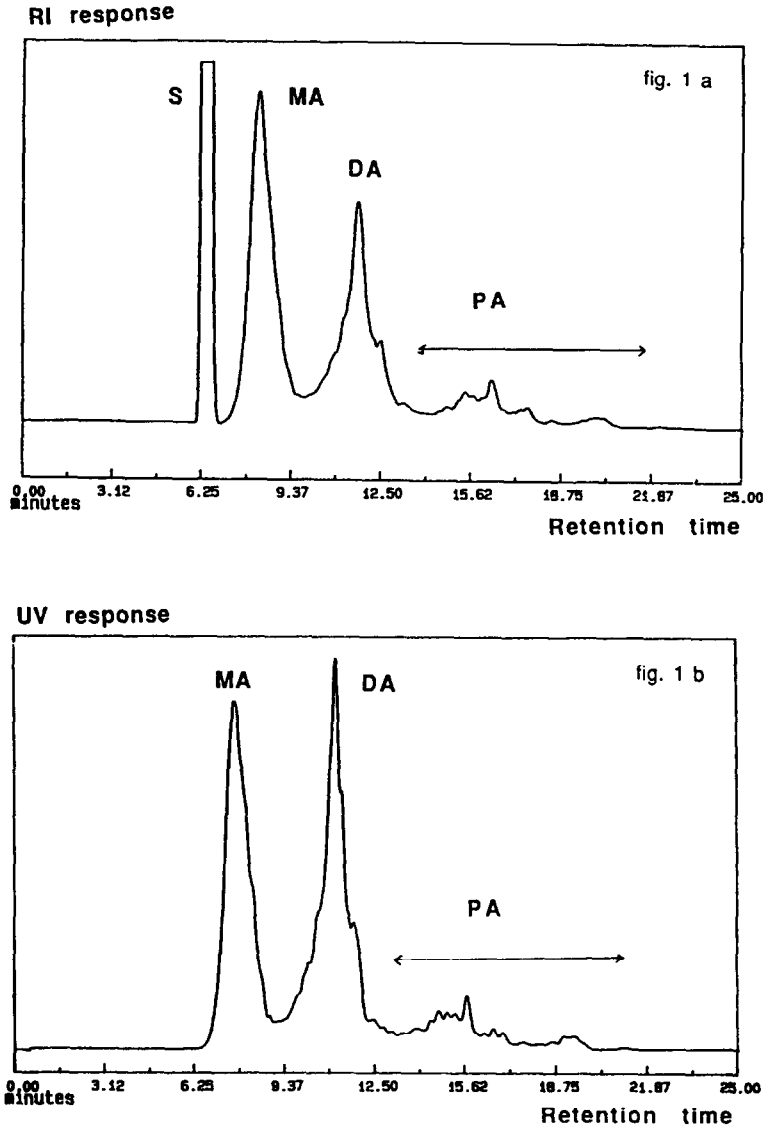

Fig. 1. Typical liquid chromatograms of a gas oil (CEN17) obtained with two aminosilica columns. (a) RI detection and (b) UV detection at 210 nm. S = saturates; MA = monoaromatics; DA = diaromatics; PA = polyaromatics.

compared with the determination using *o*-xylene, which was attributed to the presence of *n*-C_8 at low levels in the gas oil, as showed by direct GC injection of the gas oil. Consequently, only the results obtained from the HPLC aromatics fraction quantified using *o*-xylene standard were considered.

The statistical treatment of these results gave a repeatability for the total aromatics content at a level of 27% (w/w) of 3.2 and 2.6% (w/w) for the aminosilica and the silica column, respectively. The latter repeatability corresponds to a confidence interval of ±1.8% (w/w) for a single measurement. The average aromatics content of the tested gas oil was found to be 26.6 mass% (w/w) with the aminosilica column and 26.1 mass% (w/w) with the silica column. These results show a good agreement with MS measurements, i.e., 26.5 mass% (w/w) with a repeatability of 2.0%.

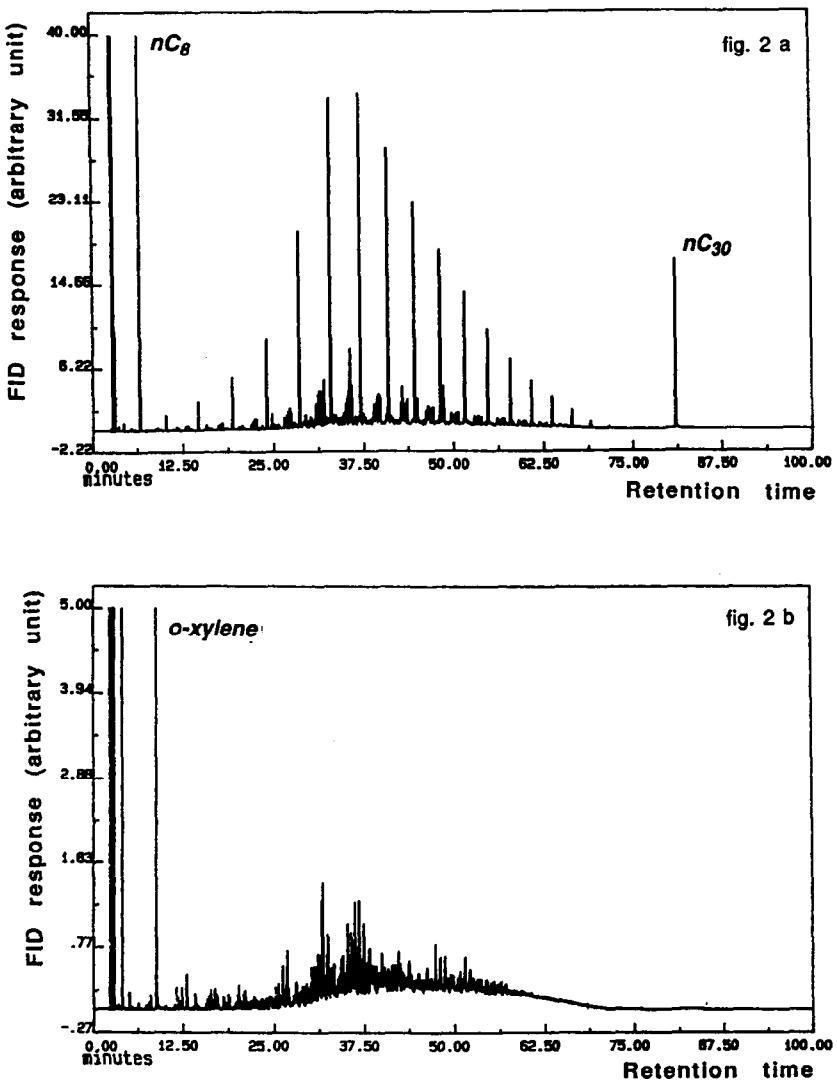

Fig. 2. Gas chromatograms of (a) the saturates and (b) the aromatics fractions of a gas oil (CEN17).

The HPLC–GC method was then used, with the aminosilica column, to determine the total aromatics content of a gas oil before and after a mild hydrotreatment. The results in Table 1 demonstrate the sample sensitivity of the ECS HPLC method and the good agreement between the HPLC–GC, MS and semi-preparative liquid chromatographic results.

The MS analysis shows that during this mild hydrotreatment a large decrease in the poly- and diaromatics content (ca. −13%, w/w) occurs whereas the monoaromatics content increases (ca. +5.5%), resulting in a decrease in the total aromatics content (ca. −7%). Results not reported in Table 1 show that after this hydrotreatment, the monoaromatics fraction contains much more C_nH_{2n-8} and C_nH_{2n-10} compounds (tetralin + indane + indene) than C_nH_{2n-6} compounds (alkylbenzenes). These C_nH_{2n-8} and C_nH_{2n-10} compounds arise from the hydrogenation of diaromatics.

The ECS HPLC method, while showing the same general trends for the three aromatic groups, does not show any significant decrease in

Table 1
HPLC–GC analysis of non-hydrotreated and mildly hydrotreated gas oils using an aminosilica HPLC column and comparison with MS, HPLC (ECS method [4]) and SA[a]

Compounds	Content (%, w/w)					
	Feed		Hydrotreated gas oil			
	MS	HPLC	MS	HPLC	HPLC–GC	SA[a]
Monoaromatics	16.4	18.5	22.0	29.4		
Diaromatics	16.5	13.2	4.6	2.9		
Polyaromatics	0.8	0.5	0.1	0.1		
Total aromatics	33.7	32.3	26.9	32.4	27.7[b]	27.5

[a] Separation of saturates and aromatics by semi-preparative LC.
[b] Average of two measurements.

the total aromatics content after hydrotreatment. It is clear from Table 1 that this is due to an overestimation of the monoaromatics content of the mildly hydrotreated gas oil. This biased result can be explained from MS analysis, which shows that *o*-xylene, the external standard for the determination of monoaromatics in the ECS method, is not well representative of the monoaromatics fraction owing to the presence of a large amount of C_nH_{2n-8} and C_nH_{2n-10} compounds in that fraction. As the differential refractive indices of tetralin and indane in *n*-heptane are ca. 0.15 compared with 0.118 for *o*-xylene (value obtained from data in ref. [10]), it is clear that the calibration with *o*-oxylene overestimates the monoaromatics content in the particular instance.

The HPLC–GC method overcomes this drawback by the use of internal standards and FID.

3.2. Kerosene analysis

The method was applied to two kerosenes, using aminosilica columns. For HPLC separation of kerosenes, the influence of the HPLC column (silica or aminosilica) on the back-flush time is much less critical as the distillation interval of these products is narrower than that of gas oils and less interferences between saturates and monoaromatics can occur.

Fig. 3 shows an example of a chromatogram for each fraction. Comparison of Fig. 3 with Fig. 2 clearly shows the influence of the distillation interval on the determination of aromatics by HPLC–GC. The narrower distillation interval of kerosenes makes the determination of the aromatics content easier as the maximum FID response for aromatics in kerosene is around 13 for ca. 14% aromatics (see Fig. 3: elution time in GC between ca. 10 and 35 min), whereas the maximum FID response for aromatics in gas oils is around 1.8 for ca. 27% aromatics (see Fig. 2: elution time in GC between ca. 10 and 75 min.). As a consequence the injected concentration of the aromatics fraction in GC for an accurate determination of the aromatics content is less critical for kerosenes than for gas oils.

The results reported in Table 2 show very good repeatability of measurements for the two samples and good agreement between aromatics content calculated from GC injection of either the saturates (using *n*-C_8 standard) or the aromatics fraction. It must be pointed out that these kerosene cuts had a high initial boiling point compared with commercial kerosenes. For commercial kerosenes the same problem as observed with gas oils would probably occur with the

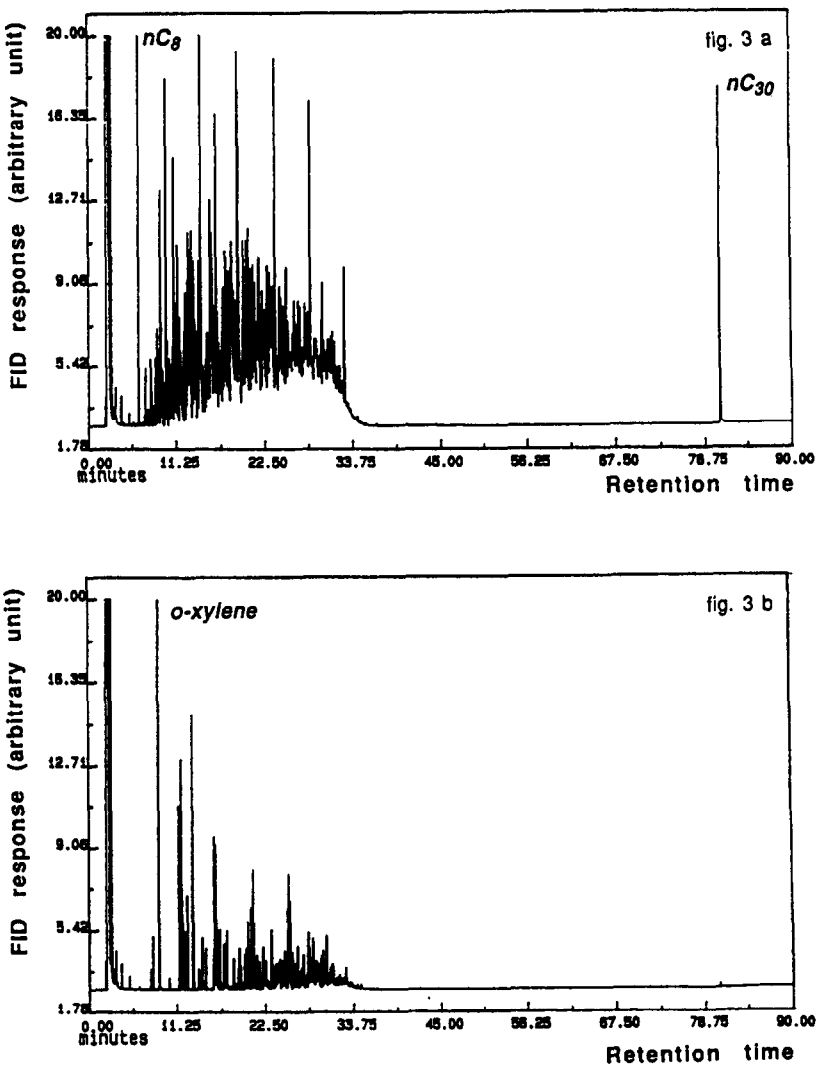

Fig. 3. Gas chromatograms of (a) the saturates and (b) the aromatics fractions of kerosene 2 (see Table 2).

determination using n-C_8 internal standard. Nevertheless, the lower final cut points of kerosenes would enable one to choose an intermediate internal standard between n-C_8 and n-C_{30} which does not interfere with the kerosene, e.g., n-C_{20}.

For the kerosene 1 samples a semi-preparative separation of saturates and aromatics was performed by liquid chromatography. The agreement between the analytical and the semi-preparative separation was very good. A comparison with the fluorescence indicator adsorption (FIAd) method [11], which gives the volume percentage, was also made and showed that, when mass percentages were calculated, taking into account the specific gravity of aromatics versus that for the whole kerosene, the FIAd method overestimates aromatics content compared with the HPLC–GC method.

On the basis of these results, we conclude that

Table 2
HPLC–GC analysis of two kerosene cuts using an aminosilica HPLC column and comparison with SA[a] and FIAd[b] methods

Method	Aromatics content			
	Kerosene 1	(b.p. 190–225°C)	Kerosene 2	(b.p. 150–250°C)
	From saturates fraction (n-C_8 internal standard)	From aromatics fraction (o-xylene internal standard)	From saturates fraction (n-C_8 internal standard)	From aromatics fraction (o-xylene internal standard)
HPLC–GC (%, w/w)	17.2, 17.0	17.3, 17.4	14.3, 14.1	14.0, 14.0
SA[a] (%, w/w)	17.1		Not measured	
FIAd[b] (%, v/v)	17.0		13.5	

[a] Separation of saturates and aromatics by semi-preparative liquid chromatography. Average of two measurements.
[b] ASTM D1319 [11].

HPLC–GC seems to be a repeatable and accurate method for the determination of the aromatics content in kerosenes and that the FIAd method probably overestimates this aromatics content. The analysis of a wider range of kerosenes will be necessary to confirm and/or generalize this point.

4. Conclusions

The off-line HPLC–GC method was evaluated for the determination of the total aromatics content in middle distillates. This method uses internal calibration and shows fairly good repeatability for both gas oils and kerosenes. We consider that this method could advantageously be used as a "reference" method for this determination in both gas oils and kerosenes. Further work is needed to determine the repeatability of the method for the whole range of aromatics content encountered in middle distillates.

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