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Routine hydrocarbon group-type analysis in refinery laboratories by high-performance liquid chromatography

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Separation of light petroleum products, with a final separation temperature of less than 315°C, into saturated, olefinic and aromatic hydrocarbons, is performed daily in all refinery test laboratories by means of the fluorescent indicator analysis method (FIA; ASTM D-1319), which consists of making a sample move under iso-propanol pressure through a column packed with silica gel, in the presence of fluorescent indicators specific to each hydrocarbon family. It has a very wide field of application, being used both for light distillation cuts and for light catalytic cycle oils (LCCO), as well as fluid catalytic cracking gasolines, olefinic cuts gasolines, etc. Aromatics with olefinic substitution, certain diolefins and molecules containing heteroatoms (S, N, O) are regarded as aromatics, which sometimes leads to confusion. Since the method is also inaccurate, time-consuming (*ca.* 2 h), and cannot be automated, refineries would appreciate a new, more reliable, quicker and if possible automatable method.

A substitution method using high-performance liquid chromatography (HPLC) was described by Suatoni *et al.* in 1975[1]. This method involves a silica column and fluorocarbon solvent (*e.g.* perfluorohexane), which has the advantage of possessing very low polarity, so that olefinic hydrocarbons can be separated from saturated hydrocarbons, and a low refractive index (1.251). When saturated hydrocarbons, then olefins, have been eluted, back-flushing is carried out to elute aromatics in a single peak, easy to integrate. A differential refractometer, calibrated with pure products, is used for detection purposes. This method was used without any modification by Miller *et al.*[2,3], who confirmed the separations obtained by Suatoni and detailed the problem of calibration, caused by the difference in response factors, and the uncertainty in the establishment of the baseline.

Recent publications have dealt with other methods. Jinno *et al.*[4] separated olefins from saturates using *n*-hexane, at a temperature of 273°K. Matsushita *et al.*[5] used silica coated with silver nitrate to separate olefins from saturates; the mobile phase is carbon tetrachloride, and infrared detection is employed. Alfredson[6] utilizes a CN column followed by a silica column; the elution is carried out with dry *n*-hexane and the detection is achieved with a refractometer and a UV detector set at 200 nm. These methods aim to replace the very expensive fluoroalkanes with more conventional solvents. However, they are more complicated than the Suatoni method, particularly for routine usage. Incidentally, it is this method that has been submitted,

without any major changes, to ASTM. A draft standard has been drawn up, and a circular test is in progress.

Clearly, once standardized, it will be adopted by all petroleum laboratories which still use HPLC only in exceptional cases. In our own company, a refinery laboratory uses it as a routine method, round the clock, using unskilled staff, to analyse widely differing products. This article describes that experience, revealing to what extent traditional methods can be easily replaced by modern instrumental methods to analyse widely different products. Quantitative results are obtained without using calibration mixtures, simply by using relative response factors calculated so that the HPLC results agree with the FIA results.

EXPERIMENTAL

Apparatus

We use a Waters apparatus consisting of a WSIP automatic injector, a M 45 pump, a RCM 100 radial compression module, a Valco back-flush valve, a R 401 refractometer, a Data Module M 730 recording and integration system, and a keyboard screen to follow the various analytical parameters. The columns are Radial-Pak silica cartridges, 10 cm long.

Reagents

The fluorocarbon mobile phase FC 72 was bought from 3M.

Procedure

Samples are injected directly into the chromatograph, through the automatic injector. Table I shows the procedural conditions applied for analysis of various products.

The column is activated simply by the passage of the mobile phase. A few column volumes are enough to ensure adequate activity to separate olefins from saturates. Back-flush is performed as soon as all olefins have been eluted, before the benzene is discharged. Back-flush duration, and thus the total time of the analysis,

TABLE I

PROCEDURE

Sample	Flow-rate (ml/min)	Quantity injected (µl)	Back-flush time (min)	Analysis time (min)
White spirit	1	8	11	25
Dearomatized white spirit	1	10	11	25
Kerosene	1	8	11	25
Dearomatized kerosene	1	10	11	25
Aromatic extract	1	6	12	30
Jet A1 fuel	1	10	12	30
Heptenes	1	8	**	14
Propylene trimers	1	8	**	16
Gasolines	1	5-8*	14	15

* Depending on saturate content.
** No back-flush.

depends on the sample. Products containing no aromatics, such as heptenes or propylene trimers, do not require any back-flushing. The refractometer is not heat-controlled. Nevertheless, a stable baseline is obtained over a whole day, by using a mobile phase that has first gone through a 0.45-μm filter, and by ensuring that the mobile phase circulates slowly in the reference cell (by gravity).

RESULTS AND DISCUSSION

Separations

A few specimen chromatograms are shown in Fig. 1. Examination shows that separations usually take place easily, except for gasolines, which require a well-activated column. We found that column performance improved with use, probably because of continuous dehydration of the stationary phase by Fluorinert. In continuous use, a column remains efficient for four or five months. Given lengths of separations, we consider mobile phase consumption reasonable, especially since the same solvent can be used several times. Greater savings can be made by using columns 2 mm in diameter, which can be used without any difficulty, or even 1 mm columns.

Calibration

Calibration was carried out by injecting samples previously analyzed by FIA, then by calculating relative response factors of saturated hydrocarbons, olefins and aromatics, from which the FIA values are found again. These factors are shown in Table II. They can be very different according to the products analyzed. All non-olefinic products can be analyzed with the same response factors, except for white spirits and aromatic extracts. Heptenes and propylene trimers do not require any response factors. All fuels can be analyzed with the same factors, except for those containing many light saturated hydrocarbons (easily recognizable by their chromatograms).

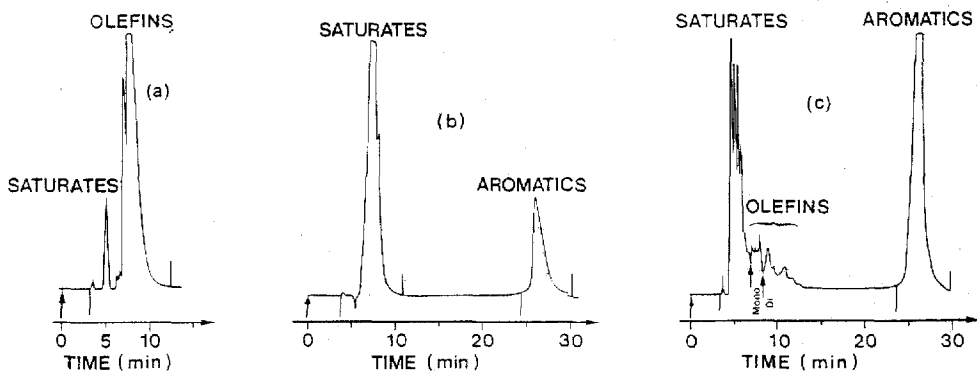For example, to analyse a fuel such as that represented in Fig. 1C, peak areas

Fig. 1. Typical chromatograms, obtained using a Radial-pak 10 × 0.40 cm I.D. column and a mobile phase of Fluorinert FC 72 at a flow-rate of 1 ml/min. (a) Heptenes, 8 μl injected; (b) white spirit, 8 μl injected; (c) gasoline, 6 μl injected.

TABLE II

RESPONSE FACTORS

Sample	Response factors		
	Saturates	Olefins	Aromatics
White spirit	1.0	*	0.6
Dearomatized white spirit	1.0	*	0.65
Kerosene	1.0	*	0.65
Dearomatized kerosene	1.0	*	0.65
Aromatic extract	1.0	*	0.7
Jet A1 fuel	1.0	*	0.65
Heptenes	1.0	1.0	**
Propylene trimers	1.0	1.0	**
Gasolines	1.3	0.95	0.4***
			0.5§

* No olefins.
** No aromatics.
*** Gasolines with light saturates.
§ All other gasolines.

of saturated (S_s), olefinic (S_o) and aromatic (S_a) hydrocarbons are measured. Corresponding percentage are calculated by using response factors shown in Table II.

$$\text{Saturates (\%)} = \frac{S_s \times 1.3}{S_s \times 1.3 + S_o \times 0.95 + S_a \times 0.5}$$

$$\text{Olefins (\%)} = \frac{S_o \times 0.95}{S_s \times 1.3 + S_o \times 0.95 + S_a \times 0.5}$$

$$\text{Aromatics (\%)} = \frac{S_a \times 0.5}{S_x \times 1.3 + S_o \times 0.95 + S_a \times 0.5}$$

We prefer this method for carrying out calibrations rather than that generally described consisting in injecting pure product blends which are too simple to account for the very various products to be analyzed. We also think that it is a risk to carry out calibrations by injecting hydrocarbon families prepared by FIA, as separations between families are not always very clear for this method.

Results

Table III lists for comparison some results obtained with both methods. In some cases, a slight difference can be noticed but we think that the correct result is obtained by the HPLC method, which is much more accurate, in particular for analyses of heptenes or propylene trimers as they contain very few saturated hydrocarbons and many olefins. However, on a whole , there is excellent agreement, which is

TABLE III

COMPARISON OF HPLC WITH ASTM D-1319

Samples		HPLC			ASTM D-1319		
		Saturates	Olefins	Aromatics	Saturates	Olefins	Aromatics
White spirit	1	82.2		17.8	82.2		17.8
	2	82.3		17.7	82.5		17.5
	3	81.9		18.1	82.5		17.5
	4	82.2		17.8	82.1		17.9
	5	82.2		17.8	81.9		18.1
	6	81.6		18.4	81.5		18.5
Dearomatized white spirit	1	96.5		3.5	96.6		3.4
	2	96.8		3.2	96.8		3.2
	3	96.8		3.2	96.8		3.2
	4	96.6		3.4	96.6		3.3
	5	96.7		3.3	97.0		3.0
	6	96.7		3.3	96.7		3.3
	7	96.1		3.9	96.1		3.9
	8	96.6		3.4	96.9		3.1
	9	96.7		3.3	96.7		3.3
	10	96.7		3.3	96.7		3.3
Kerosene	1	80.3		19.7	80.9		19.1
	2	83.9		16.1	83.9		16.1
	3	83.4		16.6	83.7		16.3
	4	80.7		19.3	81.5		18.5
Dearomatized kerosine	1	95.9		4.1	95.7		4.3
	2	96.1		3.9	95.7		4.3
	3	96.4		3.6	96.3		3.7
	4	96.2		3.8	96.0		4.0
	5	95.9		4.1	95.8		4.2
	6	96.1		3.9	96.0		4.0
	7	95.9		4.1	95.7		4.3
	8	95.6		4.4	95.8		4.2
	9	95.9		4.1	95.9		4.1
	10	96.3		3.7	96.5		3.5
	11	96.2		3.8	96.1		3.9
	12	96.5		3.5	96.4		3.6
	13	96.6		3.4	96.5		3.5
Aromatic extract	1	22.2		77.8	20.5		79.5
	2	21.6		78.4	21.2		78.8
Jet A1 fuel	1	82.5		17.5	82.5		17.5
	2	81.9		18.1	81.4		18.6
	3	82.1		17.9	82.0		18.0
	4	81.7		18.3	80.8		19.2
	4	82.0		18.0	82.4		17.6
	6	81.9		18.1	83.0		17.0
	7	82.2		17.8	82.4		17.6
	8	83.5		16.5	83.3		16.7

TABLE III (*continued*)

Samples		HPLC			ASTM D-1319		
		Saturates	Olefins	Aromatics	Saturates	Olefins	Aromatics
Heptenes	1	3.8	96.2		4.4	95.6	
	2	3.6	96.4		4.2	95.8	
	3	3.5	96.5		3.0	97.0	
	4	3.1	96.9		3.3	96.7	
	5	3.2	96.8		3.5	96.5	
	6	2.9	97.1		3.2	96.8	
	7	2.8	97.2		2.4	97.6	
	8	2.0	98.0		2.3	97.7	
Propylene trimers	1	2.9	97.1		2.2	97.8	
	2	3.1	96.9		2.2	97.8	
	3	3.3	96.7		2.6	97.4	
	4	2.7	97.3		2.7	97.3	
Gasolines	1	34.8	29.0	36.2	34.2	29.4	36.4
	2	60.3	23.7	16.0	60.5	24.2	15.3
	3	34.2	22.6	43.2	33.1	22.7	44.2
	4	49.5	23.2	27.3	51.5	23.0	25.5
	5	48.3	7.8	43.9	51.1	5.7	43.2
	6	48.5	23.4	28.1	49.1	23.0	27.9
	7	40.2	29.1	30.7	41.2	28.1	30.7
	8	40.6	28.5	30.9	41.0	29.5	29.5
	9	55.4	30.3	14.3	54.5	31.2	14.3
	10	7.1	33.9	62.5	5.1	32.4	
	11	54.3	15.3	30.4	56.2	14.6	29.2
	12	53.5	14.7	31.4	55.5	14.7	29.8
	13	60.6	11.3	28.1	60.3	13.9	25.8

clearly shown in the equations of straight correlation lines calculated from *all* the results of Table III:

FIA saturates (%) = 0.116 + 1.001 × HPLC saturates % $R^2 = 0.999$
FIA olefins (%) = −0.175 + 1.003 × HPLC olefins % $R^2 = 0.999$
FIA aromatics (%) = −0.175 + 1.000 × HPLC aromatics % $R^2 = 0.998$

CONCLUSION

HPLC is particularly well adapted to the analysis of light petroleum products in production laboratories for several reasons:
(1) The method is rapid.
(2) It can be automatized and can be used to analyse sample *series* without any intervention.
(3) Results are more reliable than those obtained by FIA.
Since the mobile phase can be recycled several times, its cost is not excessive.
In our own company, this method has been transferred without any difficulty

from the research to the production laboratory, where it has been in use round-the-clock for several months, giving complete satisfaction.

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