Journal of Chromatography, 259 (1983) 393–412
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 15,524

QUANTITATIVE ANALYSIS OF HYDROCARBONS BY STRUCTURAL GROUP TYPE IN GASOLINES AND DISTILLATES

II. LIQUID CHROMATOGRAPHY

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(First received August 5th, 1982; revised manuscript received November 12th, 1982)

SUMMARY

After summarizing the literature on the use of liquid chromatography for the analysis of petroleum samples and distillates, results are presented on the structural group type separation of gasolines by high-performance liquid chromatography (HPLC) using a perfluorocarbon mobile phase and refractive index detection. The problem of calibration, due to the difference in response factors, and the uncertainty in the establishment of the baseline are detailed. Finally, investigations on the possibility of using infrared detection for structural group type analysis by HPLC are reported.

INTRODUCTION

In Part I[1] we summarized the evolution of methods utilizing capillary gas chromatography (GC) for the analysis of complex hydrocarbon mixtures in gasolines and distillates with particular emphasis on group-type presentation of the results, and reported on our detailed investigations on the reliability of such measurements and the possibilities of utilizing computerized data handling for the presentation of the results according to different aspects. In this paper, we report on our results utilizing high-performance, elution-type liquid chromatography.

The use of liquid adsorption chromatography for the group analysis of petroleum fractions has a long history and a large number of researchers contributed to its evolution. In fact, Day, whose work may be considered as the precursor of liquid chromatography, was the first who attempted to characterize various crude oils by their group composition[2–4] and his activities were followed by a number of petroleum chemists[5]. Classical liquid adsorption chromatography has also been utilized in the systematic investigation of Research Project No. 6 of the American Pe-

0021-9673/83/$03.00

troleum Institute[6–11]. The use of liquid chromatography in petroleum analysis accelerated in the post-World War II period, and an increasing number of papers have dealt with the determination of various groups in petroleum fractions[12–21]. These activities culminated in the investigations of Snyder and co-workers in the early 1960s, resulting in both the theory of linear elution liquid adsorption chromatography[22,23] and its practical applications for group-type separation[24–29] as well as for the investigation of sulfur-, nitrogen- and oxygen-containing compounds in petroleum fractions[29–32].

The official method used worldwide in the petroleum industry utilizes classical liquid displacement chromatography with a gravity-fed column containing activated silica gel to which a mixture of fluorescent dye has been added[33]. As the petroleum fraction is separated, the dye mixture is also separated selectively, and makes the boundaries of the zones corresponding to saturated, olefinic and aromatic fractions visible under ultraviolet light. The volume percentage of each group is calculated from the length of the respective zones in the column. This method, which is generally called the FIA (*F*luorescent *I*ndicator *A*dsorption) method, is based on the studies carried out as part of API Research Project No. 6[34] as well as on the work of Conrad[35] and Criddle and Le Tourneau[36]. This method is limited to samples boiling up to 315°C but lacks precision if appreciable amounts of the sample boil above 204°C. Also, samples containing more than 5% of C_4 or more than 10% of C_4–C_5 hydrocarbons must be depentanized prior to analysis. A further disadvantage of this method is its slowness, typical of gravity-flow LC systems.

Classical liquid chromatography is also used in other ASTM methods dealing with the analysis of aromatic hydrocarbons in olefin-free gasolines[37] and in high-boiling oils[38]. In both cases, qualitative determination is based on fraction collection; in the first case, the saturates and aromatics contents are calculated from refractive index measurements in the fractions, while in the latter case, they are obtained by evaporating the solvent and weighing the residue. Again, the main disadvantage of the methods is the extended time required for the analysis.

With the evolution of modern high-performance liquid chromatography (HPLC) more accurate, reliable and faster methods for the group analysis of crude oils and petroleum products have become available. These methods, developed mainly by Suatoni and co-workers[39–42], incorporate continuous recording with a refractive index detector and backflushing of the column to facilitate the elution of aromatics as a single peak. The methods of Suatoni and co-workers, which are based on elution chromatography, are characterized by greater accuracy, shorter analysis time (around 10 min) and better group characterization: diolefins, which in the FIA method[33] elute with the aromatics, are now part of the olefin fraction (as stated by Suatoni and co-workers). In a more recent paper Alfredson[43] showed the separation of paraffins, olefins and naphthenes and aromatics in gasoline-range distillates, using a column-switching scheme incorporating silica and alkyl-bonded silica columns and an "experimental" phase whose nature was not specified.

The main difficulty of the HPLC methods is in the determination of the proper response factors: Matsushita *et al.*[44] claim that quantitation can be improved by utilizing infrared detection.

All the previous methods assume that the sample consists practically only of hydrocarbons and limit its upper boiling point. This might not be the case, however, with crude oils, and heavy petroleum distillates or residues, and analyzing such sam-

ples by the standard LC methods might result in erroneous results. Two major methods have been described for such complex samples: the method of the U.S. Bureau of Mines and the American Petroleum Institute (USBM-API Method)[45–48] and the so-called SARA (saturates, aromatics, resins and asphaltenes) method[49]. Both utilize complex systems including liquid adsorption and ion-exchange chromatography and complexation. Altgelt *et al.*[50] have discussed these techniques in detail comparing them with other schemes and methods. In a recent paper, Miller[51] described an advanced HPLC method utilizing bonded-phase liquid chromatography, and a multi-dimensional backflush technique for the analysis of crude oils, coal oils or other similar materials. Other workers have described HPLC separation techniques for higher boiling samples which employ column switching[52–55] and gradient elution[56].

Scope of this paper

The aim of our studies was to investigate, in detail, the method of Suatoni and co-workers, particularly its reliability in producing meaningful quantitative results. We also summarize the results of our investigation carried out in 1980 on the possibility of using an infrared spectrophotometer for detection.

EXPERIMENTAL

A Series 3 liquid chromatograph with a Model LC-25 refractive index detector and a Model 7125 syringe-loading injector valve (Perkin-Elmer, Norwalk, CT, U.S.A.) was used for our investigations. The column was 125 mm × 4.6 mm I.D. containing 5-μm particles of silica gel, and was activated for 2 h at 140°C under an inert gas purge. The mobile phase was Fluorinert FC-72, a fluorinated paraffin (perfluoroheptane) marketed by the 3M Company (St. Paul, MN, U.S.A.), the same substance as used by Suatoni *et al.*[39]. It has a boiling point of 50°C, a very low solvent strength ($\varepsilon^\circ = -0.25$ compared with $\varepsilon^\circ = 0.00$ for *n*-pentane) and a very low refractive index (n_D at 20°C = 1.2618). Ambient temperature was used throughout.

A Wilks Miran 1A infrared detector (Foxboro Analytical, South Norwalk, CT, U.S.A.) was used for studying the feasibility of IR detection. The column in this study was 250 × 4.6 mm I.D., packed with Partisil 10 silica gel (10 μm) activated as above. A Perkin-Elmer Model 283 IR spectrophotometer was used to obtain the spectrum of FC-72.

The liquid chromatograph was connected to a Sigma 15 Chromatography Data System with a printer/plotter to collect the raw data which were then transferred via a RS-232C communications interface to a Model 3600 Chromatography Data Station equipped with a video display unit, dual microfloppy disks and a Model 660 printer. These systems are available from Perkin-Elmer.

The gasoline samples were obtained from various commercial service stations. They were identical to the samples used in the investigations reported in Part I[1]. Individual substances used in blends or as standards were of the highest available purity.

RESULTS AND DISCUSSION

In the Introduction, we have discussed the method of Suatoni and co-workers[39–42] which utilizes an activated stationary phase and a fluorocarbon as the mobile phase and yields class separation of saturates (paraffins + naphthenes), non-aromatic unsaturates and aromatic compounds. As stated in the draft of an ASTM method now under consideration[57], aromatics with olefinic side chains, some diolefins and neutral compounds containing sulfur, nitrogen or oxygen will also be included among the aromatics. As claimed, the major advantage of the method is that results can be obtained in about 10–12 min and that individual peak identification is not needed.

The reasons why a fluorocarbon is used as the mobile phase are two-fold. First, it has a very low adsorption energy providing better separation of saturates and olefins than by a more polar mobile phase. This is best illustrated by comparison with the work of Matsushita *et al.*[44], who used carbon tetrachloride ($\varepsilon^\circ = 0.18$) and had to apply a dual column system to achieve a satisfactory separation. The second reason is the very low refractive index of the fluorocarbon increasing the sensitivity of the refractometer.

Fig. 1 shows the system used in this work. The analysis consists of two steps. First, the mobile phase is flowing in the usual way. The saturates (paraffins + naphthenes) elute as one single peak followed by a few small peaks representing the olefins. Subsequently the direction of the mobile phase is reversed resulting in a single peak for the aromatics. Fig. 2 illustrates a typical chromatogram.

The general adaptation of this method depends on its reliability which, in turn, is related to the proper response factors and the proper treatment of the baseline. These questions as well as the reproducibility of data and the correlation between results obtained by HPLC and GC were investigated in detail.

Response factors

As mentioned in Part I[1], in gas chromatography, it is generally assumed that on a flame-ionization detector, the response factors of hydrocarbons are close to each

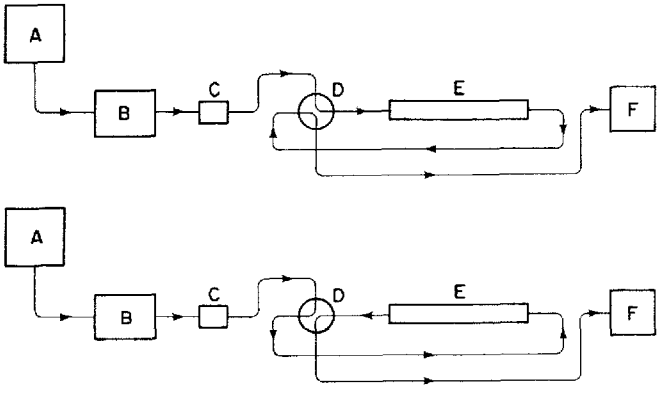

Fig. 1. Functional schematic of the HPLC system for the group analysis of gasolines and distillates. A = Mobile phase reservoir; B = pump; C = sample introduction; D = switching valve; E = column; F = detector.

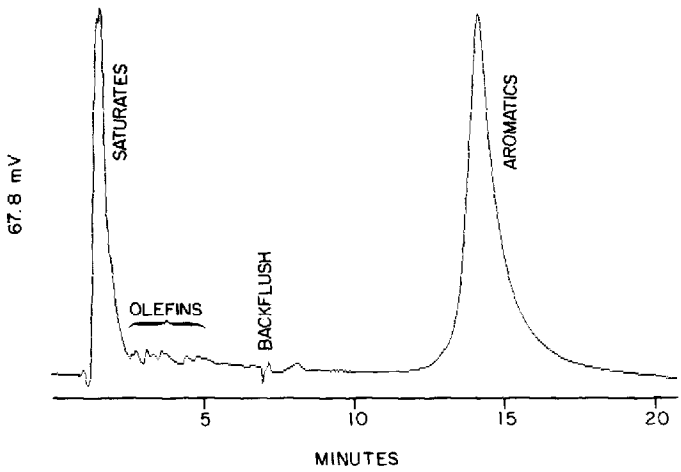

Fig. 2.Typical HPLC group analysis of a gasoline sample. Column: 125 × 4.6 mm I.D., silica gel, 5-μm particles, thermally activated at 150°C for 2 h in a nitrogen flow. Mobile phase: Fluorinert FC-72, at 2 ml/min. Ambient temperature. Backflush started at 7.00 min. Time scale (abscissa) in minutes. The full-scale deflection of the recorder (in mV) is given on the ordinate.

other. This means that relative peak area can be considered as concentration values expressed in weight per cent. This was the basis of the calculation of the concentration of the indicated compounds in the capillary GC analysis and this is also the basis of the quantitative evaluation of simulated distillation.

The situation is, however, different in liquid chromatography with a refractive index detector; here, in addition to the concentration of the particular substance in the column effluent, the detector response depends on the difference in the refractive index of the substance of interest and that of the mobile phase. This follows from the fact that the refractive index of a mixture is additive[58]:

$$n = v_1 n_1 + v_2 n_2 \tag{1}$$

where n_1 and n_2 represent the refractive indices of the pure substances, n is the refractive index of their mixture and v_1, v_2 are the respective volume fractions of the two substances in the mixture:

$$v_1 + v_2 = 1 \tag{2}$$

If n_m, n_i and n_e are the refractive indices of the pure mobile phase, the pure sample component and the column effluent, respectively, and v_m and v_i are the volume fractions of the mobile phase and the sample component in the column effluent, then

$$n_e - n_m = n_i v_i - n_m (1 - v_m) = (n_i - n_m) v_i = \Delta n v_i \tag{3}$$

where Δn represents the difference between the refractive indices of the sample component and the pure mobile phase:

$$\Delta n = n_i - n_m \tag{4}$$

In turn, the refractive index of the sample component is a function of its molecular weight (M), density (d) and molar fraction ($\mathscr{R}$)[59]:

$$n_i = \sqrt{\frac{M + 2d\mathscr{R}}{M - d}} \tag{5}$$

The molar refraction represents the sum of atomic and bond refractions and is affected by structural features in the molecule of the particular substance.

As shown, eqn. 5 also includes the density of the substance. Since the density is temperature dependent, the refractive index is also dependent on temperature. For this reason the detector cell and the connecting line must be thermostated or at least insulated.

In the HPLC method studied, a large number of compounds belonging to the same group will give one peak. In order to be able to calculate properly the concentration from the peak area we need a response factor which corresponds to the refractive index of the compounds forming the particular peak. However, the refractive index of hydrocarbons —even substances belonging to the same group— differs greatly.

Table I lists values of the refractive indices of a number of compounds, also giving the difference in the refractive index of the substance and that of the mobile phase, FC-72. As seen, the differences are significant; *e.g.*, the Δn value of *n*-octane is 1.48 times higher than that of 2-methylbutane; for octene-1 *vs.* 2-methylbutene-1 this factor is 1.93, and for cyclooctane *vs.* cyclopentane 1.36. Only in the case of aromatics is the difference minor; *e.g.*, the respective Δn values of *o*-xylene and 1,4-diethylbenzene are only 4% and 0.3% higher than the Δn value of toluene.

Because of these differences, the response factors (expressed as area counts/mg of substance) of the individual saturated and non-aromatic unsaturated compounds will be quite different (see Table II). In turn, this means that one cannot take the relative peak area directly as proportional to concentration, but the detector must be calibrated and this calibration is critical. One should prepare hydrocarbon mixtures typical of the samples of interest and use these as the standards. This is, however, a difficult question as it assumes that the saturated and olefinic groups have dominant components to permit the formulation of a standard sample using a limited number of compounds, and that these compounds and their approximate concentrations are known.

If we investigate Table III in Part I[1], the complexity of the samples and, thus, the difficulty of calibration become evident. Among the paraffins there were 16 with a concentration over 0.5% and 36 substances with even smaller concentrations. One may select a limited number of components representing the most important compounds, but a wide range of others will still be present, causing uncertainty in the

TABLE I

REFRACTIVE INDEX (n_D^{20}) VALUES OF SELECTED COMPOUNDS

The refractive index data are taken from ref. 54. The Δn values represent the difference in the refractive index of the substance of interest and that of FC-72 which is considered as perfluoroheptane (C_7F_{16}) having a refractive index of $n_D^{20} = 1.2618$.

Compound	n_D^{20}	Δn
2-Methylbutane	1.3537	0.0919
2-Pentane	1.3575	0.0957
n-Hexane	1.3751	0.1133
3-Methylhexane	1.3887	0.1269
n-Octane	1.3974	0.1356
2,2,5-Trimethylhexane	1.3997	0.1379
n-Nonane	1.4054	0.1436
n-Dodecane	1.4216	0.1598
2-Methylbutene-1	1.3378	0.0760
Pentene-2, *cis*	1.3830	0.1212
Pentene-2, *trans*	1.3793	0.1175
Hexene-1	1.3837	0.1219
Octene-1	1.4087	0.1469
Octene-2, *cis*	1.4150	0.1532
Cyclopentene	1.4225	0.1607
Cyclohexene	1.4465	0.1847
Cyclooctene, *cis*	1.4698	0.2080
Cyclopentane	1.4065	0.1447
Cyclohexane	1.4266	0.1648
1(*trans*),2-Diethylcyclopentane	1.4295	0.1677
Methylcyclohexane	1.4231	0.1613
1(*cis*),2-Dimethylcyclohexane	1.4270	0.1742
1(*trans*),2-Dimethylcyclohexane	1.4270	0.1652
Cyclooctane	1.4586	0.1968
Benzene	1.5011	0.2393
Toluene	1.4961	0.2343
o-Xylene	1.5055	0.2437
m-Xylene	1.4972	0.2354
p-Xylene	1.4958	0.2340
Isopropylbenzene	1.4915	0.2297
1,4-Diethylbenzene	1.4967	0.2349

calculation. The problem is even more obvious in the case of the olefins and naphthenes, where there are no dominant compounds present. In addition, one should not forget that the large number of unknowns, each present in very small concentrations (over 60% of them representing less than 0.1% each), will now be distributed among the four groups increasing the uncertainity. In conclusion, one can state that even the most carefully formulated standard mixture can provide only a crude approximation in the calibration.

The test sample selected by us consisted of seven components one of them

TABLE II

RESPONSE FACTORS OF SATURATED AND UNSATURATED COMPOUNDS USING A REFRACTIVE INDEX DETECTOR AND FC-72 FLUOROCARBON AS THE MOBILE PHASE

The response factor is calculated as peak area obtained on the refractive index detector, in counts, per sample weight, in mg.

Compound	*Response factor*
n-Pentane	171
n-Decane	287
2,2,5-Trimethylhexane	315
Cyclooctane	336
Cyclooctene, *cis*	432
Octene-1	256
Dodecene-1	390

representing a mixture of isomeric (C_8) olefins. Table III gives the composition of this sample, expressed in different ways. The refractive indices of the total paraffins and total aromatics were calculated according to the rule of additivity (see eqn. 1). As seen, the value for the paraffin mixture is about halfway between the refractive indices of 2-methylbutane and *n*-dodecane and the same is true about the corresponding Δn values (*cf.*, Table I). As already discussed above, the refractive indices of

TABLE III

STANDARD TEST SAMPLE USED FOR THE GROUP ANALYSIS OF PETROLEUM FRACTIONS BY HPLC

Compound	*Volume-%*	*Refractive index,* n_D^{20}	*Density (g/ml)*	*Weight (g) in 100 ml of sample*	*Weight-%*
n-Pentane	5.00	1.3575	0.6262	3.3100	4.06
2,2,4-Trimethylpentane	40.00	1.3915	0.6919	27.6760	35.90
n-Dodecane	5.00	1.4216	0.7487	3.7435	4.86
Octenes	5.00	1.4134*	0.7192*	3.5960	4.67
Toluene	15.00	1.4961	0.8669	13.0035	16.87
p-Xylene	15.00	1.4958	0.8620	12.9300	16.77
Ethylbenzene	15.00	1.4959	0.8760	13.0050	16.87
Paraffins	50.00	1.3911**		34.5505	44.82
Olefins	5.00	1.4134*		3.5960	4.67
Aromatics	45.00	1.4959**		38.9385	50.51
Total	100.00			77.0850	100.00

* Measured.

** Calculated (see text).

benzene homologs differ only very little and thus the error source here is minor. However, one still has a problem with the olefins where there is no dominant compound and thus calibration cannot be accurate.

Linearity

An important point in the use of HPLC with a refractive index detector for group analysis is the linearity of the system. The referenced ASTM text now under consideration[57] specifically requires a test for the linearity of aromatic responses by analyzing test mixtures having different concentrations and plotting the absolute peak area of aromatics *vs.* concentration.

To examine system linearity four test samples were prepared in which isooctane

TABLE IV

LINEARITY OF GROUP ANALYSIS BY THE REFRACTIVE INDEX DETECTOR

Each peak area value represents the mean of five replicate measurements. Injected volume: 5 μl.

	Aromatics (vol.%)				*Mean*	*Standard deviation*	*Relative standard deviation (%)*
	20	*40*	*60*	*80*			
	Paraffin (vol.%)						
	80	*60*	*40*	*20*			
Sample composition (μl)							
Toluene	0.333	0.667	1.000	1.333			
p-Xylene	0.333	0.667	1.000	1.333			
Ethylbenzene	0.333	0.667	1.000	1.333			
Total aromatics	0.999	2.001	3.000	3.999			
Isooctane	4.000	3.000	2.000	1.000			
Total sample	4.999	5.001	5.000	4.999			
Sample composition (mg)							
Toluene	0.289	0.578	0.867	1.156			
p-Xylene	0.287	0.574	0.861	1.148			
Ethylbenzene	0.289	0.578	0.867	1.156			
Total aromatics	0.865	1.730	2.595	3.460			
Isooctane	2.768	2.076	1.384	0.692			
Total sample	3.633	3.806	3.979	4.152			
Absolute peak area (counts)							
Aromatics	194.0582	423.6135	583.4957	751.9273			
Paraffin	602.7182	446.3165	270.9668	132.5926			
Area response factor (counts/μl)							
Aromatics	194.1	211.8	194.5	188.0	197.1	10.241	5.20
Paraffin	150.7	148.8	135.5	132.6	141.9	9.174	6.47
Area response factor (counts/mg)							
Aromatics	224.3	244.9	224.9	217.3	227.9	11.879	5.21
Paraffin	217.7	215.0	195.8	191.6	205.0	13.235	6.46

(2,2,4-trimethylpentane) represented the paraffins and an equal-concentration mixture of toluene, *p*-xylene and ethylbenzene the aromatics; the total aromatics concentration was 20, 40, 60 and 80 vol.%. These samples were analyzed on the HPLC system, always injecting 5 μl, and the absolute peak area of the peaks corresponding to the paraffin and aromatics recorded*. The detailed data are presented in Table IV.

Statistical evaluation of the absolute peak area of total aromatics and of the paraffin *vs.* concentration (in vol.%) results in respective correlation coefficients of 0.9963 and 0.9991, representing satisfactory linearity. Table IV also presents the calculated area response factor values, both as counts/mg and counts/μl. There is a considerable variation of the data, with relative standard deviation values around 6–7%, indicating the precision one may expect using a conventional integration algorithm to compute peak area. The assignment of the chromatographic baseline is the major source of variation; this question is discussed below.

Reproducibility and accuracy

Next, we evaluated the reproducibility of retention times and absolute peak area.

Retention time. As already discussed, we obtain single peaks for the saturates (paraffins + naphthenes) and the aromatics and a number of small peaks for the olefins. From the point of system reliability it is important to know the reproducibility of the retention time of the peak corresponding to the aromatics, obtained by backflushing the column. Table V presents the evaluation of the data from the measurements already reported in Table IV; again, each value represents the mean of five replicate measurements. The retention time reproducibility is very good.

TABLE V

REPRODUCIBILITY OF ABSOLUTE RETENTION TIMES

The data are from the same series of investigations as reported in Table IV. Each value represents the mean of five replicate measurements. Backflushing commenced at 3.0 min after sample introduction.

Concentration (vol.%)		*Absolute retention time (min)*	
Paraffin	*Aromatics*	*Paraffin peak*	*Aromatics peak*
80	20	1.206	5.874
60	40	1.196	5.898
40	60	1.184	5.908
20	80	1.178	5.944
Mean		1.191	5.906
Standard deviation		0.0125	0.0291
Relative standard deviation (%)		1.05	0.49

* Since there was no olefin present in this sample, backflushing was commenced at 3.0 min instead of the 7.00-min time used for samples also containing olefins.

TABLE VI

RESULTS OF REPLICATE ANALYSES OF A GASOLINE SAMPLE

Sample volume: 5 μl. For analytical conditions see the caption of Fig. 2.

Measurement	*Saturates*	*Olefins**	*Aromatics*
	Absolute peak area values (counts)		
1	39.6736	3.9992	70.3978
2	39.8166	5.3714	72.1022
3	38.6021	4.6537	69.3503
4	38.9376	5.4141	74.3602
Mean	39.2572	4.8596	71.5301
Standard deviation	0.5821	0.6713	2.2047
Relative standard deviation (%)	1.48	13.81	3.08
	Amount present (g/100 ml of sample)		
1	23.4154	1.6461	30.5769
2	23.4992	2.2109	31.3573
3	22.7830	1.9155	30.1605
4	22.9810	2.2285	32.3393
Mean	23.1697	2.0003	31.1085
Standard deviation	0.3436	0.2763	0.9588
Relative standard deviation (%)	1.48	13.81	3.08

* Sum of three peaks.

Absolute peak area. In the next step of our investigations, we evaluated the reproducibility of absolute peak area using a gasoline sample. The upper part of Table VI presents the mean values of four replicate measurements. These are typical results. Next we evaluated the same data but now, converting the peak area to g/100 ml of sample. This was done by separately analyzing a standard test sample and comparing the absolute area. If m_s is the group concentration in the test sample, in g/100 ml, A_s and A_i are the respective peak area obtained when analyzing the standard and the unknown sample, then m_i, the concentration of the same group in the unknown sample, can be expressed as

$$m_i = \frac{A_i}{A_s} \cdot m_s \tag{6}$$

The lower part of Table VI presents the results corresponding to this calculation. The reproducibility is, naturally, the same as that of the absolute peak area.

Further investigation of the data in Table VI, however, reveals a potential problem in these measurements. The sum of the means will give the weight of 100 ml

of the whole gasoline sample and, divided by 100, its density (in g/ml). The value calculated from Table VI is 56.2785, which corresponds to a density value of 0.5628. This is obviously too low for a gasoline sample; gasolines generally have densities in the range of 0.7–0.8.

There are two possible sources for this error which one will encounter on almost every gasoline sample. The first is related to the simplification in the selection of the components of the standard, resulting in a refractive index which will be different than that of the corresponding fraction in the gasoline sample. As already discussed, even the most carefully selected test sample cannot completely match the refractive indices of the gasoline fractions. A further error source is represented by the improper treatment of the baseline.

Establishment of the baseline

Improper treatment of the baseline causes particular difficulties when the concentrations of the olefinic hydrocarbons are small and the resolution from the saturates is less than perfect, which is often the case. The problem, which can be best illustrated with help of Fig. 3, representing the front part (before backflushing) of an actual chromatogram, is related to the ways a data system may establish the baseline in the case when the detector response does not return to the original baseline.

There are usually three ways a data system may establish the baseline in such a case. In the first possibility (Fig. 3A) a line representing the continuation of the original baseline prior to the peak is established and peak area is measured to this theoretical baseline ("horizontal baseline"). In the second possibility (Fig. 3B) the baseline (marked as B) is established at the beginning and end of the chromatogram

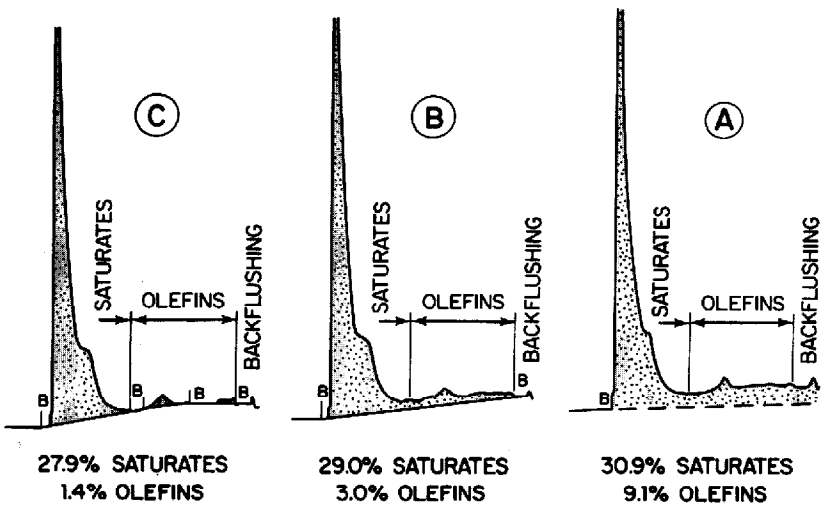

Fig. 3. Different ways to establish the baseline under unresolved peaks when the pen deflection does not return to the original baseline. A, Horizontal baseline; B, baseline from base point to base point; C, baseline valley to valley. The letters B indicate the established baselines. The small vertical lines represent the start and end of a peak while the long vertical lines indicate the windows for saturates and olefins.

or a segment of it and these are connected by a straight line and peak area is measured to this line ("base point to base point"). Finally, the third possibility for the data system (Fig. 3C) is to establish the baseline after each peak (either as a straight part or the valley between the peaks) and to connect these under each peak with straight lines ("valley to valley").

As indicated in Fig. 3 the three methods give significantly different olefin concentrations and also appreciably different values for the concentration of the saturates. However, it cannot be predicted which is the best method. This is only clear when observing the actual baselines on the video display unit (VDU) of the data station. Therefore, it is desirable to have the ability to recall the raw data, establish the best baseline on the VDU and then reintegrate the data. In addition, one should also compare in each case the density values calculated from the composition (g/100 ml) and the actual measured densities and evaluate which calculated value is closest to the latter.

In the case of the aromatics peak the problem in establishing the proper baseline is related to the difficulty of establishing the true start and end of the peak. This is illustrated in Fig. 4; as given, there is a 13% difference in the two peak area.

After establishing the composition of the sample in g/100 ml, the composition in weight percent can be calculated with help of the density of the sample determined separately:

$$\text{concentration, wt.\%} = \frac{(\text{concentration in g/100 ml}) \times 100}{\text{weight of 100 ml of sample}} \tag{7}$$

Generally, the sum of the established wt.% values will be less than 100. This is due both to the shortcomings in calibration and area loss due to the way the baseline was drawn.

Analysis of gasoline samples

We have analyzed eleven gasolines with the described HPLC method. Table VII summarizes the results obtained. In addition to the calculated concentration values, in wt.%, the table also gives the densities determined separately and those

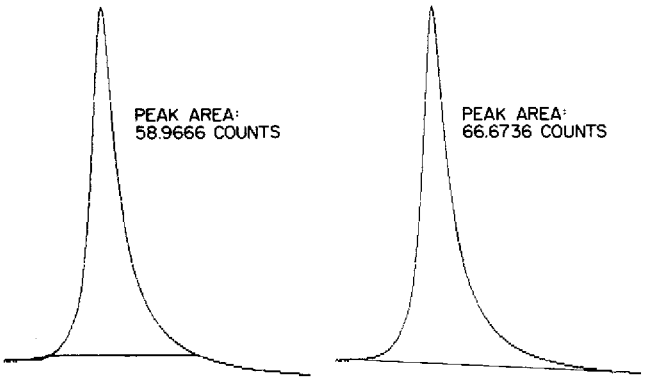

Fig. 4. Establishment of the baseline under the aromatics peak.

TABLE VII

ANALYSIS OF GASOLINE SAMPLES BY THE HPLC METHOD

For analytical conditions see the caption of Fig. 2.

Sample	*Density (g/ml)*		*Concentration (wt.%)*			
	Measured	*Calculated**	*Saturates*	*Olefins*	*Aromatics*	*"Unknowns"***
Leaded regular:						
Brand A	0.7465	0.6368	42.8	3.6	38.9	14.7
Brand B	0.7282	0.6983	46.5	9.3	40.1	4.1
Brand D	0.7420	0.6661	36.1	5.2	48.7	10.0
Unleaded regular:						
Brand A	0.7730	0.7397	38.8	6.3	50.6	4.3
Brand B	0.7092	0.7022	48.4	9.1	41.5	1.0
Brand C	0.7716	0.7212	31.3	7.1	55.1	6.5
Brand D	0.7125	0.7530	44.3	8.1	53.3	(5.7)
Unleaded premium:						
Brand A	0.7815	0.7205	29.9	4.4	57.9***	7.8
Brand B	0.7388	0.7868	43.3	8.2	55.0***	(6.5)
Brand C	0.7542	0.7198	40.8	4.4	50.3	4.5
Brand D	0.7303	0.6557	43.3	8.7	37.8	10.2

* Calculated as the sum of concentrations expressed in g/100 ml, divided by 100.

** The difference of the sum of the three wt.% values and 100.0. Value in parentheses represents value in excess of 100.0.

*** Contains about 4% methyl *tert.*-butyl ether.

calculated as the sum of the concentration value, in g/100 ml (divided by 100). The values given under "unknowns" are simply an indication of how much the sums of the three concentrations fall short of (or exceed) 100%.

It should be noted that while in capillary column GC, the additive methyl *tert.*-butyl ether will elute with cyclopentane, *i.e.*, a naphthene, here it will elute together with the aromatics. We did not correct the data for its presence.

Although the analyzed gasoline samples came from the same sources as those analyzed in Part I[1] by capillary gas chromatography, comparison of the data is very difficult. First, the samples were analyzed at different times and thus their composition might have changed. However, even more importantly, in HPLC, where one is getting a true group separation, the accurate establishment of the concentrations of the individual groups depends very much on the correct composition of the standard and the assignment of the proper baseline. The difference in the measured and calculated densities and the magnitude of the "unknowns" actually indicate the accuracy and reliability of the HPLC measurements and point to the difficulties in obtaining correct data by liquid chromatography. For this reason, we consider the capillary gas chromatography method more accurate and reliable particularly if, by additional peak identifications, the amounts of unknowns are reduced.

Naturally, by better calibration (using more complex standard mixtures) and more sophisticated establishment of the baselines, accuracy can be improved and the value of 'unknowns" reduced. However, by doing this the time of a determination, including the time needed for calibration and data manipulation, is increased and thus the method will soon lose its attractiveness as a rapid method for routine analy-

sis. This is particularly true if we consider that truly representative standard mixtures can only be prepared if the components of each group and their approximate concentration has already been established by capillary gas chromatography.

Use of IR spectroscopy for detection

As mentioned in the Introduction, Matsushita *et al.*[44], in a paper published in 1981, claimed that, by using an infrared spectrophotometer as the detector, quantitation can be improved. We have already investigated this possibility in 1980 using the same instrument, the Foxboro Analytical Wilks Miran 1A infrared detector. This is a single-beam IR spectrophotometer with a variable-wavelength filter which can either be set to a specific wavelength for a single functional group or scanned to detect various functional groups.

Here, we would like to briefly summarize our results.

Performance. In our work, we have utilized the LC system used by Suatoni and co-workers[39–42], *i.e.*, a single silica gel column and a perfluorocarbon as the mobile phase. It should be noted that Matsushita *et al.* used chloroform as the mobile phase, which does not provide separation between the saturates and the olefins; for this reason they had to use a dual-column system. In their work, the detector was set at 6.9 μm, the carbon–hydrogen deformation band, while we used the aliphatic carbon–hydrogen stretching band at 3.4 μm (2940 cm^{-1}), the most characteristic band for hydrocarbons.

Fig. 5 shows the IR spectrum of the FC-72 perfluorocarbon used by us as the mobile phase. As seen there is no transmission window at higher wavelengths but IR detection is useful below about 3.7 μm (above 2700 cm^{-1}). Thus, one can utilize the C–H stretching band at 3.4 μm. Due to slight inaccuracies in the detector setting the actual optimum wavelength on the detector used by us was at 3.46 μm (2890 cm^{-1}). Fig. 6 shows the peaks obtained at wavelengths around 3.4 μm, with the highest peaks at 3.46 μm. Due to some C–H stretch in the mobile phase (*cf.*, Fig. 5) we could not achieve zero absorbance on the detector and the % transmittance

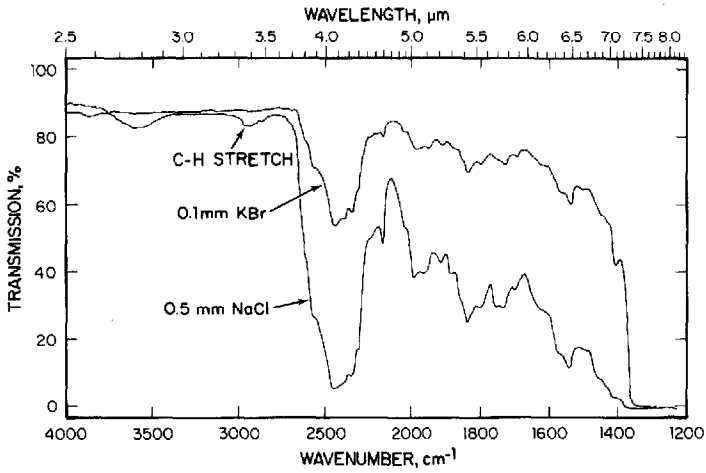

Fig. 5. IR spectrum of FC-72 perfluorocarbon. Perkin-Elmer Model 283 IR spectrophotometer with two different cells.

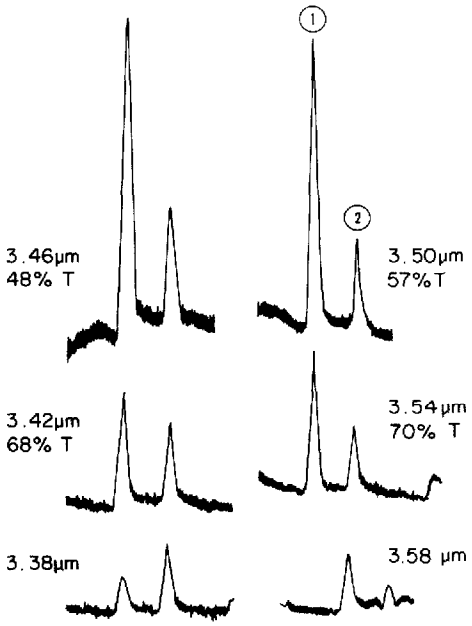

Fig. 6. IR detector response at various wavelength settings. Column: 250 × 4.6 mm I.D., Partisil 10 silica gel (10-μm particles). Mobile phase: FC-72 perfluorocarbon at 1.0 ml/min. Sample volume: 5 μl. Miran 1A IR detector with slit no. 2, time constant 1 sec, range 1 A. Peaks: 1 = cyclooctane; 2 = octadiene. The wavelengths used and the % transmittance (T) values are indicated on the figure.

values for each measurements are indicated in Fig. 6. The sample used for these and the subsequent investigation was an equivolume mixture of cyclooctane, cyclooctadiene and a diluter, the peak of which is not seen on the chromatograms.

We have also investigated the influence of a number of instrumental parameters such as the slit width and the time constant on the detector's response. As shown in Fig. 7 it is best to operate with wide slits because, although some signal enhancement is obtained when going to narrower slits, the noise also becomes increasingly greater. Increasing the time constant (Fig. 8) greatly improves the baseline while reducing the detector response to a lesser degree. However, as the time constant

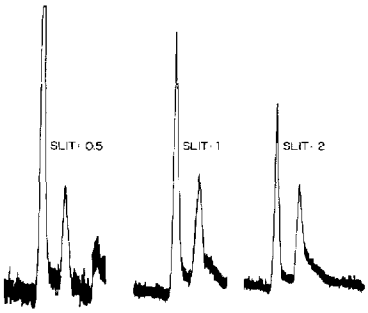

Fig. 7. IR detector response at various slit widths. Conditions as in Fig. 6. Wavelength set at 3.46 μm. The slit widths used are indicated on the figure.

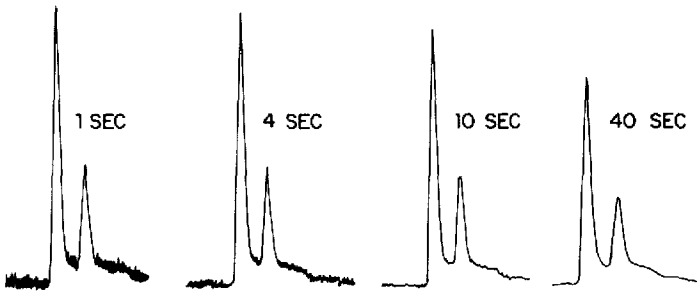

Fig. 8. The influence of the IR detector's time constant on the detector response. Conditions as in Fig. 6. Wavelength set at 3.46 μm. The time constants used are indicated on the figure.

becomes longer than the rise time of the chromatographic peak, quantitation would suffer. Time constants between 4 and 10 sec appear the best compromise.

We have also checked the linearity of the IR detector. The test samples used consisted of *n*-pentane diluted to 50 ml by toluene and a 10-μl aliquot was always injected. The results are summarized in Table VIII. As seen, the linearity is satisfactory.

We have also determined the response factors of a limited number of compounds. As indicated by Table IX, the response factors (expressed as counts/mg) are much closer to each other than those measured on the refractive index detector (*cf.*, Table II). Thus, from this point of view infrared detection would be more suitable for group analysis by HPLC. The problem, however, is that it has a much poorer detection limit than the refractive index detector.

Detection limits. Fig. 9 shows the peak obtained by injecting 1 μl of *n*-decane into the HPLC system connected to the IR detector. Calculating from this chromatogram, the signal-to-noise ratio is 39.5:1 at this time constant. Considering a peak having a height corresponding to twice the noise level, the detection limit (assuming detector linearity) would be 37 μg. At a time constant of 10 sec, the detection limit for this IR detector should be 7–10 μg and indeed, measurements with *n*-pentane at this time constant gave a detection limit of about 8 μg. This compares with a detection limit of 0.5 μg using the refractive index detector.

TABLE VIII

LINEARITY OF THE INFRARED DETECTOR

Injected volume: 10 μl. Each peak area value represents the mean of four replicate measurements carried out on two subsequent days.

n-Pentane injected (mg)	*Area (counts)*
3.3204	649.2006
1.4798	352.9728
0.8792	227.1257
0.3930	111.0336
0.1988	59.2644
Correlation coefficient (r)	0.9952

TABLE IX

RESPONSE FACTORS OF SELECTED COMPOUNDS USING AN INFRARED DETECTOR AND FC-72 PERFLUOROCARBON AS THE MOBILE PHASE

For the column see the caption of Fig. 6. The mobile phase flow-rate was 2 ml/min. Amounts of the individual compounds introduced varied between 0.8 and 1.0 mg. The response factor was calculated as the peak area obtained, in counts, per sample weight, in mg.

Compound	*Response factor*
n-Pentane	133
2,2,5-Trimethylhexane	115
n-Decane	127
Cyclooctane	150
1-Octene	85
1-Dodecene	128
Cyclooctene, *cis*	117

Matsushita *et al.*[44] gave the detection limit for olefins as 0.1% by volume. Assuming a 5-μl injection, a density of 0.75 for a typical gasoline and a density of 0.72 for the olefins, 0.1 vol.% would correspond to 3.6 μg of olefin. This is somewhat better than our result although of the same order of magnitude. One should, however, not forget that Matsushita *et al.* used a mobile phase with complete transparency at the wavelength used. As shown in Fig. 5, FC-72 had some residual band at the wavelength used by us which makes the detection limit poorer. On the other hand, as discussed earlier, we have felt that the selection of this particular mobile phase is important for separation.

The poor detectability would certainly reduce the applicability of an IR detector in the HPLC group analysis of gasolines. If we assume a density of 0.75 for a typical gasoline, then in the case of 5 μl injection, 8 μg corresponds to 0.213% by weight of the injected sample. As shown in Table III of Part I[1] among the identified olefins (a total of 20) only one was present in a concentration higher than 0.21% and among the 145 unknowns (many of which are undoubtedly olefinic) only five were

Fig. 9. Peak of 1 μl (0.73 mg) of *n*-decane obtained on the HPLC–IR detector system. For chromatographic conditions see Fig. 6. Detector conditions: wavelength, 3.46 μm; slit, no. 2; range, 1A; time constant, 4 sec.

present in a concentration higher than 0.21%. Naturally, if compounds belonging to a group elute as a single peak the responses are additive; however, at the front and end of the peak one would certainly lose compounds if the detector is not sensitive enough.

CONCLUSIONS

It is our opinion that while the infrared spectroscopic detector offers advantages in greater uniformity of detector response for paraffins and olefins, this is offset by the disadvantage of high noise and limited sensitivity.

We are somewhat skeptical about the use of HPLC for the routine determination of hydrocarbons in gasolines and similar products according to structural group types. Although the question of properly identifying all components does not arise here and the highly nonpolar perfluorocarbon mobile phase generates a true class fractionation, the proper choice of standards represents a major concern. Simple test mixtures can only represent an approximation; on the other hand, closer matching would require more detailed knowledge of the sample's composition obtainable only by a previous GC analysis. Also, the proper setting of the baseline under the peaks might require the analyst's decision at each analysis, a criterion undesired in routine analytical work.

If the HPLC method provides separation by structural groups, but one would need a separate GC analysis for better accuracy in quantitative evaluation, then an alternative approach seems to be attractive: utilization of liquid chromatography for class fractionation, and collection of the representative fractions with their subsequent gas chromatographic analysis for quantitative evaluation. Part III of our report shall deal with this possibility.

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