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Note

Rapid hydrocarbon group analysis of gasoline by high-performance liquid chromatography

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The determination of the optimal octane number for gasolines requires the accurate measurement of the amounts of saturated, olefinic and aromatic hydrocarbons present in feedstocks both before and after conversion. The analysis of these groups in the final product is also important for process control in blending gasoline.

The fluorescent indicator adsorption (FIA) method[1,2] has been used for this analysis. In this method, the hydrocarbons are separated into saturates, olefins and aromatics using a silica column operated at low pressure with isopropanol, and each type is determined by manual measurement of the bands under ultraviolet light. The FIA method is time consuming and is highly dependent upon interpretation by the analyst. Consequently, the precision is relatively poor.

High-performance liquid chromatography (HPLC) utilizes the technique developed by Suatoni *et al.*[3,4], in which the hydrocarbons are eluted from an activated silica column and detected with a refractive index (RI) detector. The method needs a back-flushing system to elute aromatics as a single peak.

This paper describes a dual-column HPLC method for the separation and determination of saturates, olefins and aromatics in gasoline. The dual-column technique uses silica gel to separate aromatics from olefins and saturates and silica gel coated with silver nitrate to separate olefins from saturates. Carbon tetrachloride is used as the mobile phase. The infrared (IR) detector used in this method provides good long-term baseline stability and thus more accurate and reproducible quantitation. The time required for a separation is 25 min without back-flushing.

EXPERIMENTAL

Materials

The gasoline samples were purchased from local service stations or obtained from a petroleum company directly. Carbon tetrachloride was of "super special" grade (Wako, Osaka, Japan). The silver nitrate-coated gel was prepared by dissolving the silver nitrate in acetonitrile, mixing the solution with LS-320 (Toyo Soda, Tokyo,

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Japan) and removing the acetonitrile on a rotary evaporator. The gel was activated at 110°C for 12 h.

Hydrocarbon group analysis was effected using a dual-column system in a Toyo Soda HLC-803B liquid chromatograph equipped with Wilks Miran-1A IR detector. The first column (50 cm × 7.5 mm I.D.) contained LS-320 silica gel (Toyo Soda) and the second column (4 cm × 7.5 mm I.D.) contained LS-320 coated with silver nitrate. Peak areas were measured with a Toyo Soda Model CP8-III computing integrator.

Procedure

Gasoline samples were injected directly into the chromatograph via the 4-μl sampling valve. The order of elution was saturates, olefins and aromatics. Without back-flushing, the aromatics were eluted within 25 min. The hydrocarbons were detected at 6.9 μm, corresponding to carbon–hydrogen functional groups. The area of each peak was integrated with the computing integrator.

RESULTS AND DISCUSSION

A typical chromatogram is shown in Fig. 1.

The columns most commonly applied for the separation of hydrocarbon group types are silica columns[3 4]. In HPLC, viscosity and miscibility considerations limit the solvents that can be used as mobile phases. An IR detector restricts the choice of solvent owing to its light absorbance characteristics. With these restrictions in mind, carbon tetrachloride was chosen as the mobile phase. Aromatics elute rapidly, although saturates and olefins are inseparable when a silica column is used with carbon tetrachloride.

Olefins can be eluted between saturates and aromatics by using the dual-column system described here. Table I shows the retention volumes of several satu-

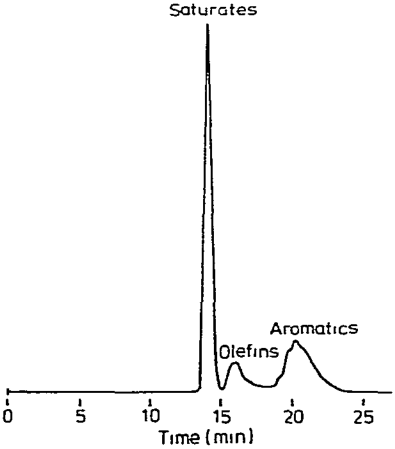

Fig. 1 Chromatogram of a gasoline without back-flushing Columns, LS-320 (50 cm × 7.5 mm I.D) and LS-320 coated with silver nitrate (4 cm × 7.5 mm I D.); mobile phase, carbon tetrachloride; flow-rate, 1.2 ml/min; sample size, 4 μl; detector, infrared

TABLE I

HPLC RESULTS FOR MODEL COMPOUNDS

Compound	*Elution time (min)*	*Relative response*	
		3.4 μm	*6.9 μm*
n-Hexane	15.4	1.00	1.00
n-Dodecane	14.8	0.99	0.79
Cyclohexane	15.5	1.13	1.78
2-Methylpentane	15.4	0.82	0.91
1-Heptene	17.4	0.71	1.10
1-Dodecene	16.8	0.90	1.02
2-Methyl-1-butene	17.9	0.43	2.12
Benzene	20.4	0.05	0.00
Toluene	20.6	0.10	0.71
p-Xylene	20.6	0.25	1.05
Ethylbenzene	20.0	0.23	0.91
1,3,5-Trimethylbenzene	21.2	0.35	1.10

* Relative to *n*-hexane = 1.00

rates, olefins and aromatics, and it can be seen that each hydrocarbon group elutes in a definite time interval.

Hydrocarbons are well suited to detection with an IR detector. A suitable wavelength having a nearly constant response for many hydrocarbons should be selected. Consequently, IR detection was employed at 6.9 μm (1440 cm^{-1}), corresponding to absorption by the carbon–hydrogen functional group. With practical samples, response factors of individual groups were determined with standard gasolines by the FIA method and, were found to be 1.000 for saturates, 0.604 for olefins and 0.941 for aromatics. The basic calculations for each group in volume percent are as follows:

$$T = \text{Area (saturates)} + 0.604 \cdot \text{Area (olefins)} + 0.94 \cdot \text{Area (aromatics)}$$

$$\%\ \text{Saturates} = \text{Area (saturates)} \cdot 100/T$$

$$\%\ \text{Olefins} = \text{Area (olefins)} \cdot 60.4/T$$

$$\%\ \text{Aromatics} = \text{Area (aromatics)} \cdot 94.1/T$$

Table II gives results for eight gasolines obtained by the FIA method and by HPLC. The results are in reasonable agreement. The detection limit for olefins by this method was determined to be 0.1 vol.-%. The accuracy and precision should be greatly improved by using a computing integrator, as this eliminates the problem of manually correcting the baseline. A computing integrator can automatically set the baseline and measure peak area over an established period. The automatically established periods were set from 12 to 15 min for saturates, from 15 to 18 min for olefins and from 18 to 25 min for aromatics.

CONCLUSIONS

A practical HPLC method for hydrocarbon group analysis of gasolines has been developped using a dual-column system. The advantages are as follows:

(1) operations are performed with no back-flushing;

TABLE II

FIA AND HPLC RESULTS FOR GASOLINES

Results are volume percentages calculated as described in the text

Sample No	*Group type**	*FIA*	*HPLC*	
			Area (%)	*Corrected (%)*
1	S	54.9	47.61	53.7
	O	16.4	24.55	16.7
	A	28.7	27.84	29.6
2	S	69.9	61.58	65.2
	O	5.4	9.72	6.2
	A	24.7	28.70	28.6
3	S	53.9	43.84	49.1
	O	16.0	22.04	14.9
	A	30.1	34.12	36.0
4	S	44.5	41.33	46.7
	O	17.8	23.99	16.4
	A	37.7	34.68	36.9
5	S	51.1	47.2w	53.2
	O	17.6	24.24	16.6
	A	31.3	28.54	30.2
6	S	52.5	40.90	47.0
	O	19.1	28.18	19.6
	A	28.1	30.92	33.4
7	S	47.2	43.85	48.7
	O	14.3	19.83	13.3
	A	38.5	36.32	38.0
8	S	52.7	46.13	52.9
	O	20.2	28.52	19.8
	A	27.1	25.35	27.3

* S = saturates, O = olefins, A = aromatics

(2) better quantitation is achieved through the use of a IR detector and a computing integrator;

(3) shorter analysis times are achieved (25 min compared with about 1 h by the FIA method); and

(4) the method could easily be applied to kerosenes.

ACKNOWLEDGEMENT

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