Instrumental Achievements

Capillary Gas Chromatography of Saturated Hydrocarbons in Gasoline by Removing Unsaturated Components by Precolumn Sulfonation

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The paraffin, olefin, naphthene and aromatic (PONA) analysis in gasoline or naphtha has long been carried out by separating the constituent hydrocarbons (HC) with a capillary column having a nonpolar stationary phase, into as many peaks as possible, followed by the peak identification and the quantification as groups.

The PONA analysis technique often encounters a serious problem in identifying hundreds of peaks obtained in a run. Even the gas chromatography/mass spectrometry (GC/MS) combined technique, which is now believed to be one of the most reliable methods for qualitative determination, can often give erroneous qualitative information on unresolved GC fractions. When the GC/MS combined technique cannot be utilized for the qualitative determination of GC fractions, it is necessary to identify GC peaks from their retention times by comparing them with those of standard pure compounds. The qualitative errors can be minimized if particular type of hydrocarbons are removed before the sample is chromatographed. We have reported the multidimensional capillary GC method (MDCGC) developed for the above purpose¹, in which the aromatics in the naphtha samples were selectively removed so that only the paraffin and naphthene peaks were recorded. The present paper refers to our experiments carried out to improve the method. Just after a gasoline sample was injected into the GC apparatus, the olefin and aromatic constituents were removed through sulfonation, so that only paraffins and naphthenes were detected on the chromatogram. Comparison of the chromatograms before and after the sulfonation makes it possible to discriminate saturated HC fractions from unsaturated ones, and to see whether a saturated HC and an unsaturated one are eluted without being separated.

Experimental

Instruments and operating conditions are listed in Table 1.

The agent to trap and remove unsaturated HCs (olefins and aromatics) was prepared in the following way. Eight grams of water and 2 g of concentrated sulfuric acid were placed in a shallow container and mixed well. Five grams of Shimalite diatomaceous

earth solid support (80–100 mesh) was added to this solution, and dried at 100°C in an oven with occasional mixing.

It is necessary to prevent sulfuric acid vapor from entering the capillary column because it would deteriorate the column. The trapping agent used for this purpose was prepared in the same way as above. Eight grams of water and 2 g of KOH were placed in a shallow container and mixed well. Five grams of Shimalite diatomaceous earth solid support (80–100 mesh) was added to this solution, and dried at 100°C in an oven with occasional mixing.

The addition type reaction of sulfuric acid to olefins and aromatics proceeds rather slowly, if the sulfuric acid contains some water. In order to accelerate the reaction, the trapping agents of unsaturated HCs were dried in the following way. In a glass tube, 2.6mm i. d. and 13 cm long, the trapping agent for unsaturated HCs was packed to a length of 3 cm and that for

Table 1 Instruments and operating conditions

Gas chromatograph	Shimadzu GC-15APFsc (dedicated to capillary GC and equipped with a temperature-controlled carrier gas flow control unit)
Attachment	CRG-15 cryogenic work attachment
Data processor	Shimadzu C-R3A Chromatopac
Column	Shimadzu HiCap CBP-1M50-025 (chemically bonded fused silica capillary column with dimethyl silicone stationary phase, 50 m long, 0.22 mm i.d., and 0.25 μ m in film thickness)
GC/MS system	Shimadzu GCMS-QP1000
Operating conditions	
Column temp.	0°C (5 min hold) to 120°C at 3°C/min
Injection temp.	120°C
Detector temp.	200°C
Detector	FID
Carrier gas	He 2 kg/cm ² , 25 cm/s
Split ratio	1/300
Septum purge flow	10 ml/min
Sample size	0.5 μ l

Fig. 1 Flow diagram of precolumn sulfonation device.

sulfuric acid vapor to a length of 1.5 cm, as shown in Fig. 1. This glass tube was connected to the sample injection port of the GC, with the trapping agent for sulfuric acid vapor at the upstream position. Then, the conditioning was carried out at 120°C with carrier gas flow for one hour.

The trapping tube described before is installed to the GC apparatus in the way shown in Fig. 1. All the parts shown in Fig. 1—pressure control valve (PC), solenoid valves (SV-1 and SV-2), molecular sieve traps (TR), and needle valves (NV-1 and NV-2)—are included in the Grob type split/splitless sample injector which is equipped with the standard GC-15APFsc gas chromatograph. The only difference is the connection of the carrier gas line to the solenoid valve.¹

The operation is made as follows.

i) Open the solenoid valve SV-1, close the solenoid valve SV-2, and allow the carrier gas to flow. The carrier gas flows into the top of the trapping tube and

Table 2 Saturated and aromatic hydrocarbons identified in the gasoline sample

Peak #	Component name	Peak #	Component name	Peak #	Component name	Peak #	Component name
1	iC4	35	223TMC5	69	3EC8	①	B
2	nC4	36	112TMCyC5	70	2MC9	②	Tol
3	iC5	37	23DMC7	71	4MC9	③	EB
4	nC5	38	2MC7	72	3MC9	④	pX
5	22DMC4	39	4MC7	73	nC10	⑤	mX
6	CyC5	40	13DMCyC6	74	5E2MC8	⑥	oX
7	23DMC4	41	3MC7	75	25DMC9	⑦	iPB
8	2MC5	42	1Mt3ECyC5	76	26DMC9	⑧	nPB
9	3MC5	43	1Mc3ECyC5	77	23DMC9	⑨	mETol
10	nC6	44	1M2t2ECyC5	78	5MC10	⑩	pETol
11	MCyC5	45	1t2DMC5	79	3EC9	⑪	135TMB
12	24DMC5	46	1c2DMCyC6	80	2MC10	⑫	oETol
13	22DMC5	47	nC8	81	3MC10	⑬	124TMB
14	23DMC5	48	11c3t4TMCyC5	82	nC11	⑭	iPB
15	33DMC5	49	1133TeMCyC5	83	5MC11	⑮	123TMB
16	CyC6	50	1M3ECyC5	84	3EC10	⑯	1MiPB
17	2MC6	51	224TMC6	85	2MC11	⑰	1M4iPB
18	3MC6	52	MCyC7	86	3MC11	⑱	INDANE
19	1t3DMCyC5	53	ECyC6	87	nC12	⑲	13DEB
20	1c3DMCyC5	54	25DMC7			⑳	1M2nPB
21	1t2DMCyC5	55	C9N			㉑	13DM5EB
22	3EC5	56	1c3c5TMCyC6			㉒	nBB
23	224TMC5	57	135TMCyC6			㉓	1M2nPB
24	nC7	58	24DMC7			㉔	14DM2EB
25	MCyC6	59	4EC7			㉕	13DM4EB
26	113TMCyC5	60	2MC8			㉖	12DM4EB
27	22DMC6	61	4MC8			㉗	12DM3EB
28	ECyC5	62	113TMC6			㉘	13DM2EB
29	25DMC6	63	3MC8			㉙	1245TeMB
30	24DMC6	64	1M3ECyC6			㉚	1235TeMB
31	1c2c4TMCyC5	65	nC9			㉛	7MINDANE
32	33DMC6	66	nC3CyC6			㉜	1M4nBB
33	123TMCyC5	67	36DMC8			㉝	1234TeMB
34	234TMC5	68	5MC9			㉞	NAPHTHALENE

i, iso; n, normal; D, di; T, tri; Te, tetra; M, methyl; E, ethyl; P, propyl; B, butyl; c, cis; t, trans; Cy, cyclo; Tol, toluene; X, xylene; o, ortho; m, meta; p, para; N, naphthene. C4, butane; C5, pentane; C6, hexane; C7, heptane; C8, octane; C9, nonane; C10, decane; C11, undecane; C12, dodecane.

Fig. 2A Chromatogram of Gasoline.

Fig. 2B Chromatogram of saturated hydrocarbons removed after removing the unsaturated hydrocarbons by precolumn sulfonation.

toward the capillary column, in the same way as in the ordinary capillary GC. The flow rate in the septum purge line is 10 ml/min and that at the split vent is 300 ml/min. Cool the column oven to 0°C and inject 0.5 µl of the sample.

ii) At 30 s after sample injection, close the solenoid valve SV-1 and open the solenoid valve SV-2. The carrier gas flows through the SV-2 and enters the trapping tube from the bottom and flows toward the capillary column. At the same time, the carrier gas flows upward through the trapping tube and prevents the products formed in sulfonation and the sulfuric acid vapor from flowing into the capillary column.

iii) Determination of sulfonation temperature: The sulfonation which is a gas-phase reaction must occur instantaneously. Our experiment showed that olefins were sulfonated instantaneously at 80°C but that aromatics were not sulfonated rapidly enough; especially the sulfonation of benzene required the higher temperature of 120°C. The 3 cm long trapping agent can be used up to 10 injections of 0.5 µl gasoline sample.

iv) The analysis of the original gasoline samples was carried out using the same flow line, with its trapping tube replaced with an empty glass insert. The other operational conditions were the same as mentioned above.

Results and Discussion

Figure 2A shows a chromatogram of a gasoline sample from which no components have been removed, and Fig. 2B shows that of a sample from which olefins and aromatics have been removed. Those peaks that are found in Fig. 2A but not in Fig. 2B correspond to unsaturated HC fractions. The saturated HCs were identified with the Shimadzu GCMS-QP1000 and through retention time comparison using pure standard compounds. Table 2 shows the results of qualitative determination of the main saturated HCs and aromatic HCs.

Comparison of the Fig. 2A and Fig. 2B shows:

- i) Olefins are eluted close to *n*-paraffins of the same number of carbon atoms.
- ii) A series of branched paraffins are eluted before corresponding *n*-paraffins in a certain order, for example, peak #38–41 before #47 (*n*-octane), peak #60–63 before #65 (*n*-nonane), peak #68–72 before #73 (*n*-decane), peak #78–81 before #82 (*n*-undecane), peak #83–86 before #87 (*n*-dodecane).
- iii) Contents of olefins eluted after *n*-octane are minor.
- iv) Comparison of peak heights in Fig. 2A and Fig. 2B shows that 1-*trans*-3-dimethyl-cyclopentane (peak #19), 2,2,4-trimethylpentane (peak #23), 1-methyl-*cis*-3-ethylcyclopentane (peak #43) 1-*cis*-2-dimethylcyclohexane (peak #46), 1,1-*cis*-3-*trans*-4-trimethylcyclopentane (peak #48) are co-eluted with olefin fractions.

Reference

1. K. Shiomi, *Anal. Sci.*, 1, 327 (1985).

(Received April 23, 1987)

(Accepted May 25, 1987)