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Column switching–back flushing technique for the analysis of aromatic compounds in gasoline

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Abstract

A simple method, based on the technique of capillary column switching–back flushing, has been developed for the detailed analysis of aromatic compounds in gasoline. The sample was first separated on a 30-m long OV-2330 polar precolumn and then backflushed onto a nonpolar analytical column. The early eluting components from the precolumn and the components of interest (aromatic compounds plus heavier compounds) eluting from the analytical column are all directed to the same flame ionization detection system through a T piece, which permits the quantitative analysis of aromatic hydrocarbons in gasoline by a normalization method using correcting factors. The switching time window of the method is ± 5 s, resulting in easier operation and higher reliability. The reproducibility of the quantitative analysis was $\leq 3\%$ RSD for real gasoline samples.

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1. Introduction

The analysis of aromatic compounds, especially the benzene content, is fundamental to the quality control of gasoline. The instrumental requirement for the minimum detectable concentration of benzene in gasoline is in the 30–100 ppm (v/v) range at present, and will be at the ppm (v/v) level in the near future. Conventional methods [1–5] using a long capillary PONA (Paraffines, Olefines, Naphthenes and Aromatics) column for the separation and analysis of

aromatic compounds in gasoline suffers from a large number of interfering substances, particularly when the concentrations of the target components are low.

The type of hydrocarbons in oil products is determined using a standard method of fluorescent indicator adsorption [6] or nonstandardized on-line coupled capillary LC–capillaryGC techniques [7]. The former method has several limitations [8], while the latter one could not analyze samples of low boiling points such as gasoline. The technique of multidimensional gas chromatography [9,10] and column switching strategies [11–13] is effective for the analysis of a group of specific analytes in a complex matrix, and has been applied to analyze the components of interest in oil products. Among these techniques, multivalves, multicolumns and even the

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traps were employed for the group separation and the detailed analysis of components in each group [14,15]. With a very polar precolumn, aromatic compounds are retained far behind the aliphatic compounds of similar volatility, and are then switched into a nonpolar column for detailed analysis. Since the early eluting components of the sample are prevented, external or internal standards have to be used for quantitative work, resulting in tedious work and poor repeatability when manual operations are carried out.

The present study shows a simple method based on the technique of capillary column switching–back flushing for the analysis of gasoline. Both the early eluting substances and the components of interest are all directed to the same detector through a T piece, which permits the quantitative analysis of aromatic hydrocarbons in gasoline by a corrected normalization method.

2. Experimental

2.1. Instrumental set-up

A Shimadzu gas chromatograph 14A (Shimadzu, Japan) equipped with a split/splitless injector and a flame ionization detection (FID) system was used. The split-ratio was 1:30. A chromatographic workstation (KeFen, Dalian Institute of Chemical Physics, China) was used for data processing. The flowchart of the device is shown in Fig. 1. Nitrogen was used as the carrier gas and auxiliary gas, both of which were in the constant flow mode. A six-port Valco valve (VICI, USA, $T_{\max}=225^{\circ}\text{C}$) was employed as the switching valve. The precolumn was a $30\text{ m}\times 0.32\text{ mm I.D.}\times 0.3\text{ }\mu\text{m OV-2330}$ fused-silica capillary column (Restek, USA) and the analytical column was a $30\text{ m}\times 0.53\text{ mm I.D. } 1.2\text{ }\mu\text{m OV-1 FS}$ capillary column (KeFen). A narrow-bore capillary tubing of $4\text{ m}\times 0.20\text{ mm I.D.}$ was used for resistance matching. A low dead volume tee of SST316 with bore size 0.8 mm was specially made for the device (shown in Fig. 2).

2.2. Reagents and samples

Analytical-reagent grade benzene, toluene and xylenes were purchased from Aldrich. A prepared

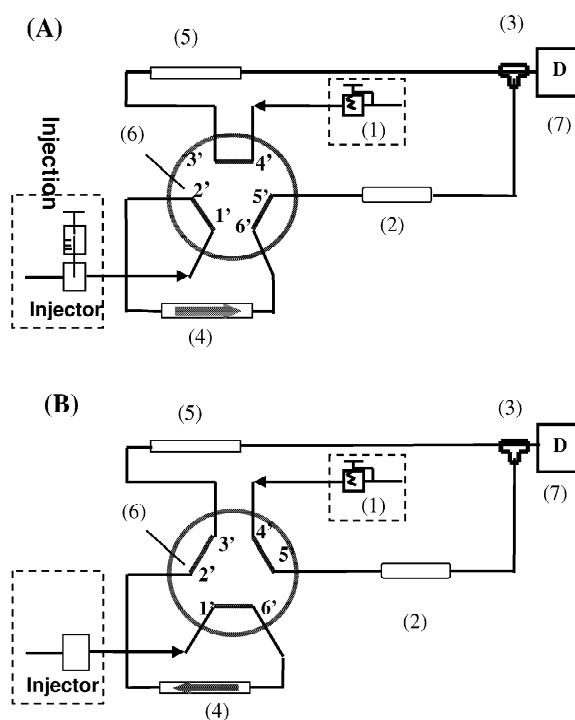


Fig. 1. Schematic diagram of the column switching–back flushing system: (A) flow chart before valve switching. (B) flow chart after back-flushing. (1) flow controller; (2) resistor tubing; (3) T piece; (4) precolumn; (5) analytical column; (6) switching valve; (7) FI detector.

mixture of these compounds was spiked in pentane. Fujian Refinery and Chemical of China provided gasoline samples.

2.3. Operation procedure

The sample injected was first introduced into precolumn through a valve (shown in Fig. 1A). The aliphatic components ($\leq n\text{-C}_{10}$) soon eluted from the precolumn and passed through a resistor and reached FID detector through a T piece. Meanwhile, the auxiliary carrier gas purged the analytical column and vented into the T piece, acting as a make-up gas for the precolumn. After the elution of $n\text{-C}_{10}$, the valve was switched and the aromatic compounds were back flushed into analytical column for detailed separation (Fig. 1B). The effluent was directed into the FID system through the T piece, where the

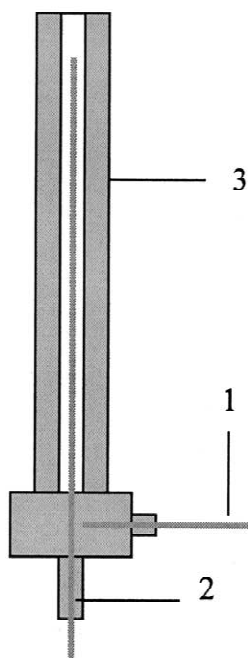


Fig. 2. Illustration of the micro-Tee. 1=End of analytical column; 2=end of resistor; 3=narrow-bore I.D. tubing to FI detector.

carrier gas passing through the resistor and reaching the T piece played as a make-up gas for analytical column.

The operation conditions were follows: 40 °C for 3.5 min, then 25 °C/min to 100 °C, and finally 8 °C/min to 150 °C hold for 10 min. The temperature of injector and detector was 280 °C. The flow-rates of the carrier and auxiliary gases were 1.8 and 2 ml/min, respectively.

3. Results and discussion

The column switching technique has been previously applied to the analysis of the complex petrochemical samples [10–15]. A very polar precolumn and a nonpolar analytical column is generally used in the two-dimensional mode, where the group of aliphatic compounds is separated from other groups based on the polarity difference, while the separation in the second dimension is based on volatility. Since only target components are introduced into the FID

system in most applications, external or internal standards have to be employed for quantitative work. Multi-injection operation and prolonged analysis time are unavoidable in this case, and can lead to poor accuracy and repeatability of analytical results when manual operations are employed. In addition, when a short micropacked column of OV-2330 or TCEP is used as precolumn, in which the resolution of group separation is just enough and the time-window of group cutting to be granted is limited to 0.2–0.4 s, large error of both quantitative and qualitative analysis can be generated when column retention has a little shift.

In our study, a capillary column with a high-polarity OV-2330 phase was used for group separation. Benzene was retained after n -C₁₀, and all the other aromatic compounds were eluted after n -C₁₁. The 30-m long capillary column results in a wide time window for valve switching since the retention distance between benzene and n -C₁₀ was as much as 12 s, which permits a ± 5 s error of cutting in practical operation. The aromatic compounds and heavier aliphatic compounds ($\geq n$ -C₁₁) were back flushed into the second nonpolar column for detailed analysis. The oven temperature was programmed at 25 °C/min immediately after the valve switching to 100 °C in order to sharpen the chromatographic band before it entered the second column. A thicker film, 1.5 μ m, OV-1 phase analytical column was selected instead of the standard 0.6–0.8 μ m film thickness in order to separate benzene and the rest of the aromatic compounds from each other even at an oven temperature of 100 °C and above.

The micro-tee performed a very important role in the method. When the effluent from one of the columns was directed to the detector, the gas flow from the other channel acted as make-up gas, which thereby eliminated dead volume and avoided peak tailing. Because all the peaks from both columns were detected on the same detector under the same conditions, normalization method with correcting factors could be employed for quantitative analysis, which simplified the routine analysis of benzene and other aromatic compounds in gasoline.

The chromatogram of the standard mixture is shown in Fig. 3. The baseline is undisturbed by valve switching. All the peaks were well separated, showing a minor broadening-effect of the back flushing operation. In comparing the analytical results of

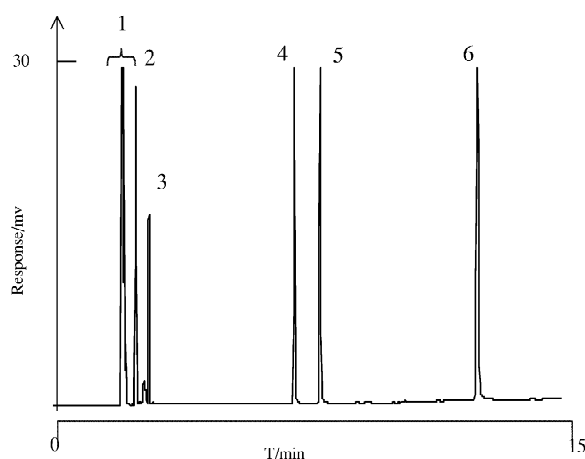


Fig. 3. Chromatogram of standard mixture. Peaks: 1=solvent; 2=*n*-nonane; 3=*n*-decane; 4=benzene; 5=toluene; 6=*n*-dodecane.

standards in single precolumn with that of the above-mentioned method (shown in Table 1), the recoveries were almost identical, which proved that there was no sample losses during the process of valve switching.

The analysis of a gasoline sample produced by catalytic cracking process was completed in 15 min, and the resulting chromatogram is shown in Fig. 4. Identification of all the peaks was based on standards. Benzene, toluene and xylenes were well separated from others, which can be determined accurately with the normalization method using correcting factors. The correcting factors of components were obtained by the determination of standards, and the correcting factors of group com-

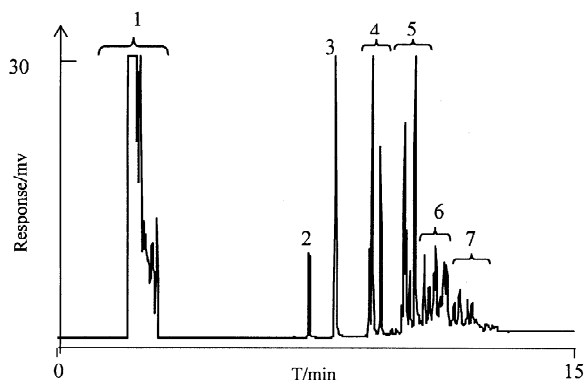


Fig. 4. Chromatogram of catalytic gasoline. Peaks: 1=saturated compounds ($\leq C_{10}$); 2=benzene; 3=toluene; 4=xylene; 5=trimethylbenzene; 6=tetramethylbenzene and methylethylbenzene; 7=saturated compounds ($\geq C_{11}$).

ponents were averaged (shown in Table 2). Heavier aromatic compounds such as C_{9+} and C_{10+} were basically group separated. The saturated compounds with similar boiling points as C_{9+} were eluted before *n*- C_{10} on the precolumn, it is impossible for components other than aromatic compounds to interfere with the C_{9+} group. Although there was a little overlap between C_{10+}/C_{11+} aromatic compounds and heavier aliphatic compounds, little error could be yielded on the total amount of aromatic compounds since their concentrations were very low. However, the method is primarily applied to the analysis of benzene, toluene and xylenes in gasoline since their toxicity is much more serious than that of other compounds, and they are under control by the regulation of government. To verify the allowable error of switching time, different switching time at 2.80, 2.85, 2.90, 2.95 and 3.00 min was employed. The results in Table 2 indicate that the time window for the valve switching is ± 5 s when the error of quantitative analysis is 4% RSD. The analysis of reformed gasoline sample is demonstrated in Fig. 5. The identification and quantification of peaks are similar to the method mentioned above. Large peaks of aromatic compounds were clearly separated from the other components, showing that the method is suitable both for low and high contents of aromatic compounds. The results of the two samples are in good agreement with the data obtained by the ASTM

Table 1

Comparison of the quantitative results obtained with a single precolumn (S) to those with column switching-back flushing technique (T)

	Composition and the weighed factor normalization result (% , w/w)				
	<i>n</i> -Nonane	<i>n</i> -Decane	Benzene	Toluene	<i>n</i> -Dodecane
S	11.43	4.25	8.92	9.71	12.28
T	11.71	4.13	8.68	9.55	12.61
R	11.12	4.08	8.90	9.90	12.90

R, the real weighed content of components.

Table 2
Influence of switching time on the quantitation results of aromatic content in the analysis of catalytic gasoline

Switching time (min)	Composition and content (% , w/w)				
	Benzene	Toluene	Xylene	Trimethylbenzene	Tetramethylbenzene, methylethylbenzene
2.80	0.66	6.60	5.73	5.51	5.26
2.85	0.62	6.43	5.88	5.50	5.11
2.90	0.65	6.83	5.71	5.71	5.01
2.95	0.69	6.61	5.57	5.47	5.18
3.00	0.68	6.20	5.82	5.70	4.96
Average content	0.66	6.53	5.74	5.58	5.10
Average correcting factor	1.00	1.04	1.10	1.12	1.14
RSD (%)	4	4	2	2	2

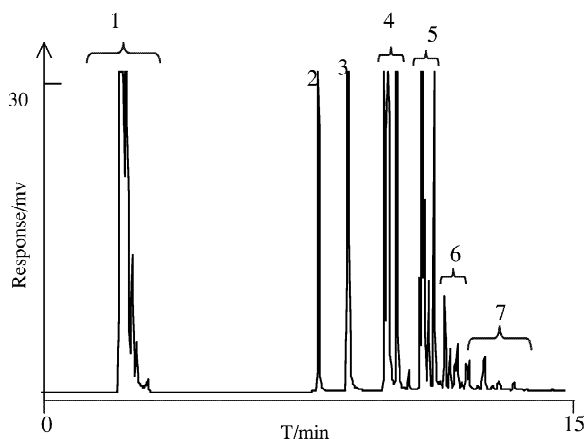


Fig. 5. Chromatogram of reformed gasoline. Peak identification: 1=saturated compounds ($\leq C_{10}$); 2=benzene; 3=toluene; 4=xylene; 5=trimethylbenzene; 6=tetramethylbenzene and methylethylbenzene; 7=saturated compounds ($\geq C_{11}$).

method D 4420-89 as shown in Table 3, which were supplied by the refinery plant.

4. Conclusion

This study provides a simple and reliable method to determine the total amount of aromatic compounds, especially benzene, toluene and xylenes, by one injection and a correcting factors weighted normalization method. User-friendly operation and short analysis time have been realized. The total analysis time was within 15 min for each sample. The two streams of carrier gas entering the T piece acted as make-up gas for each other, eliminating the dead volume effects of the connector.

Table 3
Comparison of the content of aromatic hydrocarbons in catalytic gasoline (A) and reformed gasoline (B) determined with the new method and the standard ASTM method

	Composition and average content (% , w/w)				
	Benzene	Toluene	Xylene	Trimethylbenzene	Tetramethylbenzene, methylethylbenzene
A	0.66	6.53	5.74	5.58	5.10
A ^a	0.70	6.60	6.02	5.20	–
B	4.56	14.30	22.90	13.70	3.20
B ^a	4.79	14.70	23.60	12.80	–

^a The refinery plant provided the data according to the method of ASTM D 4420-89.

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