

การวิเคราะห์ปริมาณเบนซีนและโทลูอีนในน้ำมันเบนซิน ด้วยวิธีก๊าซโครมาโทกราฟีและการประยุกต์ใช้

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บทคัดย่อ

พัฒนาวิธีการวิเคราะห์หาปริมาณเบนซีนและโทลูอีนในน้ำมันเบนซินด้วยวิธีการที่ง่ายและใช้ระยะเวลาสั้นในการวิเคราะห์ โดยใช้เครื่องแก๊สโครมาโทกราฟี หัววัดชนิด FID และคอลัมน์ DB-1 วิเคราะห์ตัวอย่างน้ำมันเบนซิน ออกเทน 91 และ 95 จากสถานีบริการน้ำมัน 3 ยี่ห้อจำนวนทั้งหมด 46 สถานี สารเบนซีน และโทลูอีนในน้ำมันเบนซิน ปรากฏพีคที่เวลา 4.87 และ 8.60 นาที ตามลำดับ วิธีวิเคราะห์นี้สามารถวิเคราะห์เบนซีนและโทลูอีนได้ด้วยความเข้มข้นร้อยละ 0.012 และ 0.049 โดยปริมาตร ตามลำดับ การวิเคราะห์เบนซีนที่ความเข้มข้นร้อยละ 3.00 และ 4.66 โดยปริมาตรในน้ำมันเบนซิน ให้ค่าความถูกต้องร้อยละ 99.00 และ 106.01 โดยมีค่าสัมประสิทธิ์ความแปรปรวนน้อยกว่าร้อยละ 9.00 การวิเคราะห์โทลูอีนที่ความเข้มข้นร้อยละ 5.95 และ 9.92 โดยปริมาตรในน้ำมันเบนซิน ให้ค่าความถูกต้องร้อยละ 103.36 และ 93.65 โดยมีค่าสัมประสิทธิ์ความแปรปรวนน้อยกว่าร้อยละ 4.00 ค่าเฉลี่ยของเบนซีนในน้ำมันออกเทน 91 และ 95 เป็นร้อยละ 1.69 ± 0.49 และ 1.55 ± 0.41 โดยปริมาตร ตามลำดับ ส่วนค่าเฉลี่ยของโทลูอีนในน้ำมันออกเทน 91 และ 95 เป็นร้อยละ 7.23 ± 2.47 และ 7.01 ± 1.78 โดยปริมาตร ตามลำดับ ความเข้มข้นของเบนซีนและโทลูอีนในน้ำมันเบนซิน 3 ยี่ห้อที่ศึกษามีค่าแตกต่างกันอย่างมีนัยสำคัญทางสถิติ

คำสำคัญ : เบนซีน, โทลูอีน, น้ำมันเบนซิน, ก๊าซ-ลิควิดโครมาโทกราฟี

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DETERMINATION OF BENZENE AND TOLUENE IN GASOLINE BY GAS-LIQUID CHROMATOGRAPHY AND IT'S APPLICATION

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Abstract

A simple and rapid method for determination of benzene and toluene in gasoline was developed by using gas chromatograph with flame ionization detector and a commercial DB-1 capillary column. The method was used for analyzing gasoline octane 91 and 95 collected from three brands of 46 gasoline service stations. The method separated benzene and toluene in gasoline at retention times of 4.87 and 8.60 min, respectively. The method could detect benzene and toluene at 0.012 and 0.049 % by volume, respectively. The accuracy of method for determining 3.00 and 4.99 % by volume of benzene in gasoline was 99.00 and 106.01 % respectively with the covariance of variation of less than 9 %. The accuracy of method for determining toluene in gasoline at the concentration of 5.95 and 9.92 % by volume was 103.36 and 93.65 % respectively with the covariance of variation of less than 4. The result showed average benzene in gasoline octane 91 and 95 were 1.69 ± 0.49 % and 1.55 ± 0.41 % respectively and toluene concentrations in gasoline octane 91 and 95 were 7.23 ± 2.47 % and 7.01 ± 1.78 % respectively. The concentrations of benzene and toluene in gasoline in the three brands studied were significantly different.

Keywords: benzene, toluene, gasoline, gas-liquid chromatography

Introduction

Gasoline is a complex mixture of volatile hydrocarbons, predominantly in the C4-C12 range, with a boiling point range of 50-200 °C.

The composition of total aromatic hydrocarbon for typical automotive gasoline is approximately 31%, specifically 3.2% benzene and 4.8 % toluene¹. The benzene concentration in gasoline in Thailand is usually defined by government

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regulation. The concentration of toluene in gasoline was not defined due to moderate toxicity. Benzene concentration shall not be more than 3.5% and aromatic hydrocarbon not more than 35% by volume². Short-term exposure to benzene may have respiratory tract irritation, skin and eye irritation, dizziness, headache and narcotic. Long-term exposure to a high concentration of benzene induces hemopoietic toxicity and increases the risk of cancer because benzene has been identified as a human carcinogen or leukemia causing agent³. Toluene can cause impairment of coordination and momentary loss of memory (200-500 ppm); palpation, extreme weakness and pronounced loss of coordination (500-1500 ppm)⁴.

While benzene exposure in the workplace is decreasing, petroleum containing a few percent of benzene has become an important source of benzene exposure⁵. In previous studies, the analysis of benzene and toluene in gasoline was carried out using switching-back flushing technique⁶, comprehensive two-dimensional gas chromatography⁷ and ASTM standard method⁸. The ASTM method used the following three columns in order; 10% OV101 on Chromosorb PAW 80/100, 20% TCEP on Chromosorb PAW 80/100 and 15% Carbowax 1540 on Chromosorb W. These methods are expensive and troublesome requiring complicated instrument. This research developed the method for analyzing benzene and toluene in gasoline using a commercial DB-1 capillary column equipped with

flame ionization detector with short analysis time.

Materials and Methods

Chemicals

Benzene and carbon disulfide, analytical grade, were purchased from Merck (Darmstadt, Germany). Toluene was purchased in analytical grade from APS Ajaz Fine Chem., Australia. 2,2,4 - Trimethyl pentane and n-heptane were analytical grade from Lab-scan Analytical Science, Thailand.

Instrumentation

The Shimadzu GG- GC-2010 gas chromatograph (Shimadzu, Kyoto, Japan) with a DB-1 capillary column (30 m x 0.25 mm I.D. (J&W, USA), equipped with a flame ionization detector was used. The carrier gas was helium at a flow-rate of 1.2 ml/min. The condition for analysis of benzene and toluene in gasoline was 40°C for 9 min, ramped up to 250°C at 40°C/min and hold for 5 min; injector, 275°C; detector, 275°C with a split ratio of 100.

Preparation of standard solutions

For the standard stock solution, 0.02 ml benzene and 0.04 ml toluene was diluted to 10 ml with carbon disulfide in a volumetric flask. The benzene and toluene concentrations in this stock solution were 17.55 and 34.50 mg/ml respectively. The calibration curve of benzene and toluene were prepared at 0.44, 0.88, 1.76, 3.51, 5.26 mg/ml and 1.73, 3.45, 6.90, 13.80, 20.70 mg/ml respectively.

Method validation

Known concentrations of benzene and toluene were prepared in a mixture of n-heptane and isooctane (1:1 ratio) at the concentrations of 2.63, 4.39 mg/ml for benzene and 5.18, 8.63 mg/ml for toluene. Then, 0.1 milliliter of known concentrations of benzene and toluene mixed with 0.9 ml carbon disulfide and 1 μ l was injected into the GC. The experiment was carried out for three replications. The detection limit of benzene and toluene in gasoline reported using the concentration that gives a signal three times the standard deviation of background.

Sample collection at gasoline service stations

Three brands of 46 gasoline service stations in Bangkok area were selected. Gasoline octane 91 and 95 in gasoline service stations were collected from filling nozzles into glass bottles on the sampling day. The bottles of gasoline octane 91 and 95 were stored in the laboratory at -35°C until analysis.

Analysis of benzene and toluene in gasoline

A 0.1-ml gasoline was mixed with 0.9 ml carbon disulfide and the solution was shaken slightly and 1 μ l was injected into the GC system using solvent flush technique. All gasoline samples were duplicate analysis. The percentages by volume of benzene and toluene in gasoline were calculated from the calibration curve plotted using concentrations of benzene and toluene versus their integrated peak areas.

Statistical analysis

Descriptive statistic was used for summary of all data. The concentrations of benzene and toluene in gasoline octane 91 and 95 in these three brands were compared using one-way ANOVA. Due to inequality of variance, Brown-Forsythe was used and if it is significantly different, and then Post Hoc multiple comparisons of Tamhane were used.

Results

Chromatogram of benzene and toluene in gasoline

The chromatogram of standard benzene and toluene in carbon disulfide showed benzene and toluene peaks separated at the retention time of 4.87 and 8.60 min, respectively (Fig 1). Chromatograms of blank and commercial gasoline sample were presented in Fig.2 and 3 respectively. The blank sample showed a small amount of signal at the retention time of benzene. In gasoline sample, a lot of interference peaks were found on the chromatogram, but benzene and toluene peaks were resolved from the other peaks within 30-min analysis time.

Calibration curves of benzene and toluene in gasoline

The calibration curves of benzene and toluene in gasoline showed a linear relationship between the peak area of chemicals and chemical concentrations. The correlation coefficients of calibration curve of benzene and toluene in gasoline ($n = 3$) were 0.9983 and 0.9970, respectively (Table 1). The detection limits of benzene and toluene in gasoline were 0.012 and 0.049 % by volume, respectively.

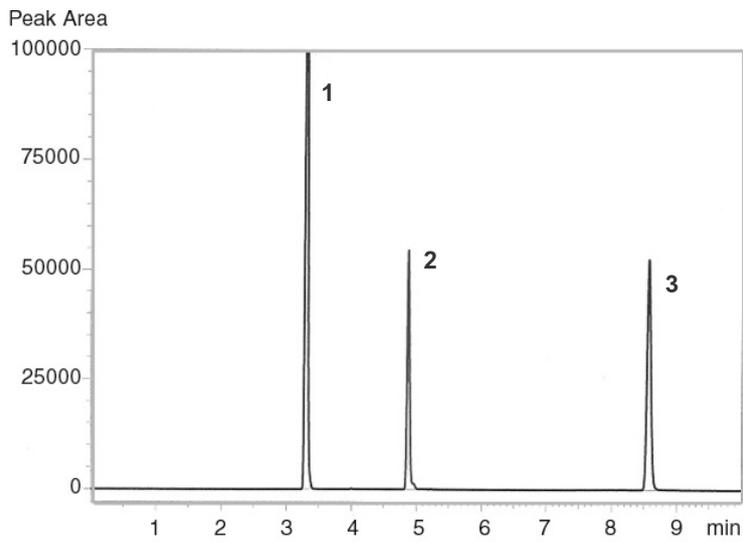


Fig. 1 Chromatogram of standard benzene and toluene in carbon disulfide; 1 = CS₂, 2= Benzene and 3 = Toluene

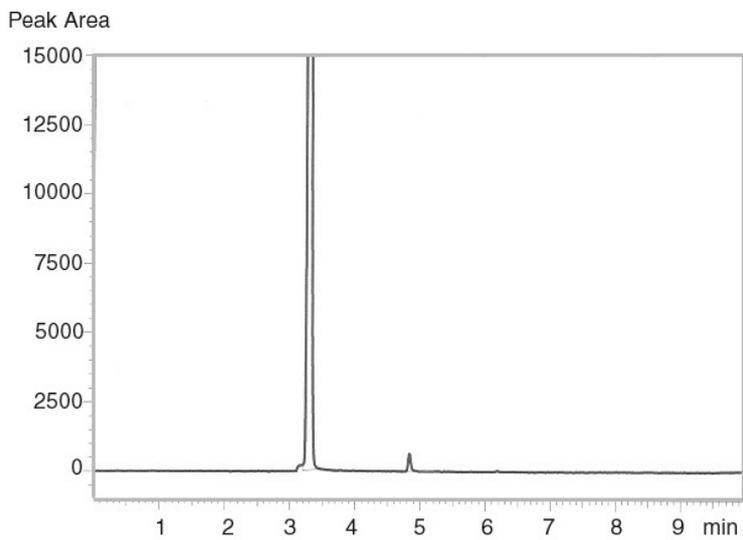


Fig. 2 Chromatogram of blank carbon disulfide

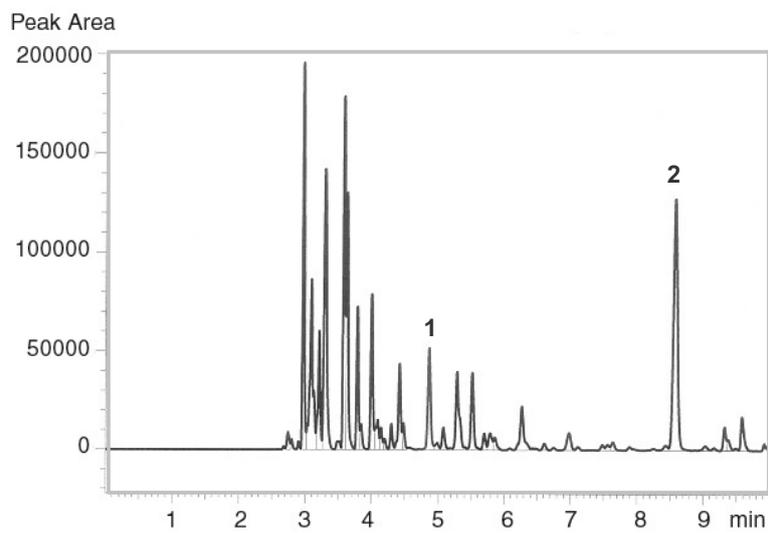


Fig. 3 Chromatogram of gasoline 95 sample showing benzene (1) and toluene (2) peaks

Method validation

Known concentrations of benzene and toluene in the mixture of heptane and isooctane (1:1 ratio) were analyzed for three replications by the studied method and presented in Table 2. The chromatogram of mixture of heptane and isooctane spiked with benzene and toluene was presented in Fig.4. The accuracy of method for determining 3.00 and 4.99% benzene in gasoline was 99.00 and 106.01%, respectively with the covariance of variation of less than 9%. The

accuracy of method for determining toluene in gasoline at the concentration of 5.95 and 9.92% by volume was 103.36 and 93.65%, respectively with the covariance of variation of less than 4.

Gasoline samples collection at gasoline service stations

This study collected gasoline octane 91 and 95 at 46 gasoline service stations. Of these, 30 stations (65.22%) were collected from brand A; 11 stations (23.91%) from brand B, and 5 stations (10.87%) from brand C.

Table 1 Calibration data

Compound	Range (% v/v)	Slope	Y-Intercept	R ²
Benzene	0.50 – 5.98	0.2201	0.0301	0.9983
Toluene	1.98 – 23.80	0.2698	- 0.0952	0.9970

Table 2 Average accuracy and precision of known benzene and toluene concentrations in a mixture of heptane and isooctane solution

No.	Benzene (% by volume)				Toluene (% by volume)			
	Actual	Estimated	Accuracy (%)	%CV	Actual	Estimated	Accuracy (%)	%CV
1	3.00	2.97 ± 0.26	99.00	8.75	5.95	6.15 ± 0.24	103.36	3.90
2	4.99	5.29 ± 0.14	106.01	2.65	9.92	9.29 ± 0.14	93.65	1.51

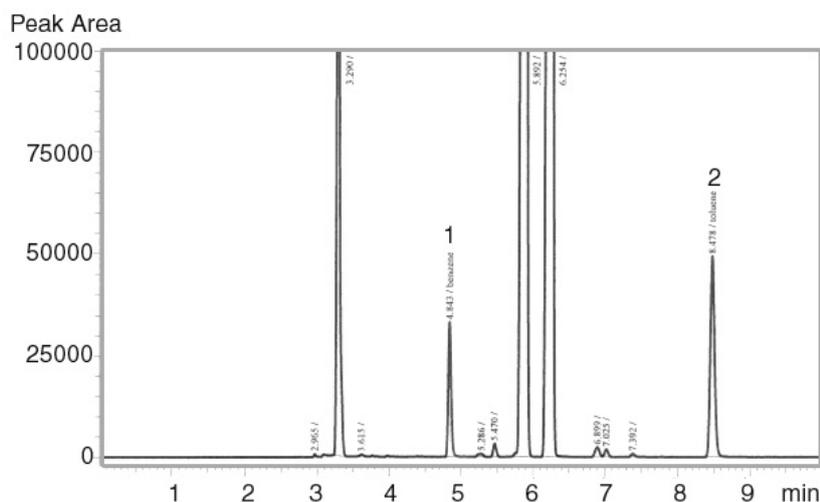


Fig. 4 Chromatogram of a mixture of n-heptane and isooctane (1:1 ratio) spiking with benzene and toluene showing benzene (1) and toluene (2) peaks.

Benzene concentrations in gasoline

The average benzene concentration in gasoline octane 91 of the three brands studied was 1.70 % by volume ranging 0.79 - 2.69 % (Table 3). Comparison among the three brands studied (A, B and C) showed that benzene concentrations in gasoline octane 91 in brand A were significantly different from those in brand B ($p < 0.001$) and those in brand C ($p = 0.015$), and benzene concentrations in brand B and C were significantly different ($p = 0.002$) at 95% confident limit (Table 4). Brand B had highest benzene concentration while brand A had lowest concentration.

With regards to gasoline octane 95, the average benzene concentration in gasoline octane 95 was 1.56 % by volume ranging 0.72-2.46%. Concentrations of benzene in gasoline octane 95 from brand A were significantly different from those in brand B ($p < 0.001$) and not significantly different from those in brand C ($p=0.890$), and benzene concentrations in brand B and C were significantly different ($p = 0.007$) at 95% confident limit. Brand B had highest benzene concentration.

Toluene concentrations in gasoline

The average toluene concentrations in gasoline octane 91 were 7.23 % by volume ranging 2.96 - 18.52% (Table 3). The comparison of toluene in gasoline octane 91 among the three brands studied showed that the toluene concentrations in brand A were significantly different from those in brand B ($p \leq 0.001$) and

those in brand C ($p = 0.020$) but the toluene concentrations in brand B and C were not significantly different at $p = 0.138$ (Table 4). Brand C had highest toluene concentration while brand A had lowest concentration.

With regards to gasoline octane 95, the average toluene concentrations in the three brands were 7.01 % by volume ranging 2.85 - 11.27%. The comparison of toluene in gasoline octane 95 among the three brands studied showed that the toluene concentrations in brand A were significantly different from those in brand B ($p < 0.001$) and those in brand C ($p < 0.001$) but the toluene concentrations in brand B and C were not significantly different at $p \leq 0.099$. Brand C had highest toluene concentration while brand A had lowest concentration.

Discussion

The experimental design intended to collect the same amount of samples from these three brands. At the beginning of sample collection, the government promoted the use of gasohol to replace gasoline. Brand B and C had started selling gasohol during that period. The number of service stations of brand B and C was reduced, because the researcher decided to collect samples in service station without gasohol. In that period of time, gasoline service stations with gasohol were not popular. The researcher intended to collect gasoline samples to be the representative gasoline sold in Bangkok area.

Table 3 Average benzene and toluene in gasoline

Gasoline	n	Mean \pm S.D.	Range
Benzene			
91 (% by volume)	46	1.70 \pm 0.49	0.79 – 2.69
95 (% by volume)	46	1.56 \pm 0.41	0.72 – 2.46
Toluene			
91 (% by volume)	46	7.23 \pm 2.47	2.96 – 18.52
95 (% by volume)	46	7.02 \pm 1.78	2.85 – 11.27

Table 4 Percentage by volume of benzene and toluene in gasoline 91 and 95

Brand	n	Benzene in gasoline (% by volume)			Toluene in gasoline (% by volume)		
		Mean	Range	P-value	Mean	Range	P-value
Gasoline 91							
A	30	1.42	0.79 - 2.08	<0.001 ¹	5.84	2.96 - 7.54	< 0.001 ³
B	11	2.33	1.84 - 2.69		9.01	7.88 - 10.69	
C	5	1.72	1.52 - 2.07		12.51	10.79 - 18.52	
Total	46	1.69	0.79 - 2.69		7.23	2.96 - 18.52	
Gasoline 95							
A	30	1.40	0.72 - 1.99	<0.001 ²	6.20	2.85 - 8.63	< 0.001 ⁴
B	11	1.95	1.36 - 2.46		8.24	6.01 - 9.85	
C	5	1.45	1.30 - 1.62		9.52	8.34 - 11.27	
Total	46	1.55	0.72 - 2.46		7.01	2.85 - 11.27	

Remarks:

1. Benzene concentrations in brand A were significantly different from those in brand B ($p < 0.001$) and those in brand C ($p = 0.015$). Benzene concentrations in brand B and C were significantly different ($p = 0.002$).
2. Benzene concentrations in brand A were significantly different from those in brand B ($p < 0.001$) and not significant different from those in brand C ($p = 0.890$). Benzene concentrations in brand B and C were significantly different ($p = 0.007$).
3. Toluene concentrations in brand A were significantly different from those in brand B ($p \leq 0.001$) and those in brand C ($p = 0.020$) but toluene concentrations in brand B and C were not significantly different at $p = 0.138$.
4. Toluene concentrations in brand A were significantly different from those in brand B ($p \leq 0.001$) and those in brand C ($p < 0.001$) but toluene concentrations in brand B and C were not significantly different at $p \leq 0.099$.

The method for determining benzene and toluene by GC could separate benzene and toluene peak with short analysis time of 30 minutes. The method validation followed the method of Singh⁹ by spiking known concentrations of benzene and toluene into the mixture of heptane and isooctane (1:1 ratio) gave reliable results. The accuracy of method for determining 3.00 and 4.99 % benzene in gasoline was 99.00 and 106.01 %, respectively with the covariance of variation of less than 9 %. The accuracy of method for determining toluene in gasoline at the concentration of 5.95 and 9.92 % by volume was 103.36 and 93.65 %, respectively with the covariance of variation of less than 4. Therefore, this study method was reliable and could be used as alternative method for analysis of benzene and toluene in gasoline. However, this method also has limitation by using one DB-1 capillary column.

Regarding the analysis of benzene and toluene in gasoline, the range of benzene and toluene in gasoline octane 91 was 0.79 - 2.69 and 2.96 - 18.52 % by volume, while the range of benzene and toluene in gasoline octane 95 was 0.72 - 2.46 and 2.85 - 11.27 % by volume, respectively. At present, government regulation stated that the benzene concentration in gasoline should not more than 3.5%. Therefore, these three companies were compliance with the government standard.

Most benzene and toluene in gasoline octane 91 and 95 from three brands of gasoline service stations found significant difference. The different benzene and toluene concentrations may result

from different refinery plants, and different sources of crude oil.

At present time, the government promoted the use of gasohol, ethyl alcohol was used to mix with gasoline at 10%. Then, the benzene content in gasoline was reduced for only 0.1%. Since, benzene has been proofed to be a confirmed human carcinogen; the use of benzene should be reduced to a minimum. In western countries, benzene concentration in gasoline was controlled at 1% following the government regulation, but Thai regulation stated that the benzene concentration should be less than 3.5 %. The alternative way to reduce benzene and toluene exposure for service attendants is to reduce the benzene and toluene concentration in gasoline. Thai government should considered reducing the quantity of benzene and toluene in gasoline to protect service station workers' health and to conserve overall natural environment. In addition, control of vehicle exhaust emissions is one of the effective controls of air pollution from traffic. If the gasoline contains a lesser amount of benzene and toluene, the overall amount benzene and toluene in the atmosphere will be significantly reduced.

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