

A GC Method for the Quantitative Determination of BTEX in Gasoline

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Abstract

A gas chromatographic (GC) method for the routine quantitation of benzene, toluene, ethylbenzene, and xylene isomers (BTEX) in gasoline is described. This method is an alternative to the direct injection of gasoline into the GC system via a split injector. A weight-based sample and standard preparation procedure is applied to overcome the error involved with a volume-based procedure (i.e., error due to the evaporation of light fractions). Quantitative analysis is performed using an internal standard method. Linearity is evaluated for each aromatic hydrocarbon, and correlation coefficients vary from 0.999174 to 0.999736. Precision and accuracy are evaluated.

Introduction

Motor vehicle traffic represents one of the most critical problems in urban areas because it causes significant harmful effects on health and environment. The most important toxic effects are related to the presence of carcinogenic and/or mutagenic substances or mixtures in the exhaust gases. The International Agency for Research on Cancer (IARC) classifies exhaust gases from vehicles with diesel engines under class 2A (probably carcinogenic to humans) and emissions from vehicles with gasoline engines under class 2B (possibly carcinogenic to humans) (1). Benzene is by far the most harmful of the substances contained in gasoline and in exhaust gases. It is considered to be carcinogenic to humans on the basis that it has been associated with an increased incidence of acute myeloid leukemia in workers who had been repeatedly exposed to high airborne concentrations of benzene (2–6). In particular, IARC has classified benzene under class 1, (i.e., among the substances that are clearly proven to be tumor inducing in human beings) (7). The assumption that a carcinogen can be active even at very low dose levels has given rise to concern that benzene in ambient air may be responsible for a portion of the incidence of leukemia in the general population; an evaluation of the number of tu-

mors originated by the exposure to benzene from motor vehicle traffic in Milan, Italy in 1993 has already been performed using a simple model (8). The result obtained was congruous with the 300 leukemia death cases recorded during 1 year in Milan (9).

Benzene in motor gasoline in Europe is controlled so that it does not exceed a maximum of 5% by volume, whereas in Italy the current average is 3%, which is subsequent to the agreement stipulated in 1992 among Unione Petrolifera and the Ministries of Health, Industry, Public Transports and Environment.

Therefore, it is interesting to observe benzene concentration levels in gasoline distributed inside urban areas and in the atmosphere. A decreasing trend in annual average airborne concentrations of benzene has already been observed in Milan (10), and this is mainly ascribable to benzene reduction in fuels.

The necessity to design a method for the determination of aromatic hydrocarbons (AHs) in gasoline derived from several considerations: (a) American Society for Testing and Materials (ASTM) methods (11–13) could not be used in our laboratories because of the particular requirements relative to the instrumentation needed. (b) ASTM method D 2267, dismissed in the United States but still in use in Europe, was inadequate because it was used for the analysis of distillates containing low concentrations of olefinic hydrocarbons and no oxygenated additives (14). (c) An easily applicable method was needed. (d) Reporting of precise and accurate data was required. Hence, direct split injection of gasoline was avoided, and a meticulous operative protocol regarding sample and standard preparation procedures was outlined. (e) Finally, we thought that, because of the toxicological implications both for workers and for the general population related to the presence of benzene in gasoline, fuels should be controlled by public prevention laboratories even though petroleum industries can autocertify their products. This is important mainly when an agreement between public administrations and producers regarding mean and/or maximum concentration levels of some compounds (e.g., benzene and sulfur) in fuels is achieved. This is the situation in many Italian cities (e.g., Milan, Rome, and Turin) where the principal Italian producer distributes gasoline and diesel fuel with reduced benzene and sulfur contents, respectively.

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In this report, we describe the method developed and present the results of linearity, precision, and accuracy assessments.

Experimental

Reagents and chemicals

Benzene, toluene, ethyl benzene, and *o*-, *m*-, and *p*-xylene were obtained from PolyScience (Niles, IL). Chlorobenzene was provided by Merck (Darmstadt, Germany). Carbon disulfide for the determination of volatile organic compounds was obtained from J.T. Baker (Phillipsburg, NJ).

Apparatus

A Mettler PL3000 technical balance, a Sartorius 1801 analytical balance, 20-mL headspace vials (DANI; Monza, Italy) with butyl/poly(tetrafluoroethylene) septa and aluminum locking nuts, and gastight syringes (Hamilton; Reno, NV) were used for sample and standard preparation.

ASTM densimeters (84H and 85H) and a thermometer (12C/IP64) were used to carry out density measurements.

The gas chromatographic (GC) system consisted of a Hewlett-Packard (HP) model 5890 series II GC equipped with an HP 7673 autosampler, an on-column injector, and a flame-ionization detector. Data were acquired with an HP 3365 series II Chemstation and worked out with an HP Vectra 486/33VL computer using Microsoft Excel version 4.0a.

Method

A weight-based sample and standard preparation procedure was applied to overcome the errors due to volume measurement at ambient temperature (possible evaporation of compounds with lower boiling points, one of which is benzene). Hence, preparation of all the following solutions was performed by using airtight 20-mL headspace vials. The operation was as follows. The vial, together with the locking nut and septum, were tared on an analytical balance; then the solvent (either carbon disulfide or the internal standard [ISTD] solution) was added, the vial was closed, and the weight of the solvent was determined. The solvent was always added so that it filled about three-quarters of the vial volume, which corresponded to 20–24 g. The weights of all substances added after this step were accurately determined. Hereafter, only the solvent used will be specified.

Preliminary trials were carried out to verify the tightness of the septa after single and multiple punctures. Having confirmed adequate tightness even after 3 h from last puncture, we prepared the standard and the sample solutions using chlorobenzene as the ISTD.

Furthermore, the weight-based sample preparation procedure allowed us to keep the gasoline at -18°C until its use, thus limiting evaporation of the lighter fractions.

Preparation of the ISTD solution

A concentrated ISTD solution (approximately 10 mg/g) in carbon disulfide was pre-

pared. It was then diluted to obtain the final ISTD solution (approximately 400 $\mu\text{g/g}$) used in the preparation of the calibration solutions and for the dilution of gasoline. The preparation of the diluted ISTD solution was carried out as follows. A screw-capped bottle of dark glass was tared using a technical balance, and approximately 200 g of carbon disulfide and the concentrated ISTD solution were added; the headspace vial was accurately washed with carbon disulfide. The washing liquid was then poured into the bottle, and solvent was added to make up 500 g.

Preparation of the calibration solutions

A concentrated solution (S_{conc}) of benzene, toluene, ethyl benzene, and xylene isomers (BTEX) in carbon disulfide was prepared. The approximate concentration of each AH is reported as follows: benzene, ethyl benzene, and *o*- and *p*-xylene, 300 $\mu\text{g/g}$ each; *m*-xylene, 600 $\mu\text{g/g}$; toluene, 1200 $\mu\text{g/g}$.

The concentration ratio among the AHs reflects that observed in gasoline.

Six calibration solutions (C_1 – C_6) were prepared by diluting a previously calculated quantity of S_{conc} with carbon disulfide and adding approximately 0.3 g of the ISTD solution. The approximate concentrations of each AH in the calibration solutions are listed in Table I.

Benzene concentrations in solutions C_3 and C_4 (central points of the calibration curve) represent the average percent-by-weight amounts found in gasoline; the linearity was evaluated in the range 0.3–9.0 $\mu\text{g/g}$ (equivalent to the same range expressed as percent by weight in gasoline), which includes benzene levels in real samples.

Sample collection and preservation

Gasoline samples were taken both in fuel stores and fueling stations. Gasoline was delivered in a cold metal container (1-L capacity) that was immediately closed with an airtight stopper. In fueling stations, gasoline was taken after a refueling was made to avoid sampling of gasoline that had remained for a long time in the pipe (with possible evaporation of the lighter fraction). Samples were kept refrigerated and, once in the laboratory, were preserved at -18°C until use.

Sample preparation

Gasoline was first diluted with the ISTD solution to obtain a solution (D_1) containing about 10 mg/g gasoline. Afterward, an aliquot of the D_1 solution was diluted with carbon disulfide to obtain a solution (D_2) containing about 100 $\mu\text{g/g}$ gasoline and

Table I. Approximate Concentrations of Benzene, Toluene, Ethylbenzene, and Xylene Isomers in the Six Calibration Solutions

Aromatic hydrocarbon	Concentration ($\mu\text{g/g}$)					
	C_1	C_2	C_3	C_4	C_5	C_6
Benzene	0.3	0.75	1.5	3.0	6.0	9.0
Toluene	1.2	3.0	6.0	12.0	24.0	36.0
Ethylbenzene	0.3	0.75	1.5	3.0	6.0	9.0
<i>p</i> -Xylene	0.3	0.75	1.5	3.0	6.0	9.0
<i>m</i> -Xylene	0.6	1.5	3.0	6.0	12.0	18.0
<i>o</i> -Xylene	0.3	0.75	1.5	3.0	6.0	9.0
Chlorobenzene	4.0	4.0	4.0	4.0	4.0	4.0

about 4 $\mu\text{g/g}$ chlorobenzene. A 1- μL aliquot of the D₂ solution was injected into the GC system for the quantitation of BTEX.

Density measurement

Density measurements were carried out in a cold storage room (+4°C). The temperature of the sample during the density measurement was recorded so as to render possible the conversion of the measured density values into the corresponding ones at 15°C and to allow the expression of results as percent by volume.

GC analysis

A CP-Wax 52CB column (25 m \times 0.25-mm i.d., 0.2- μm film thickness) from Chrompack (Raritan, NJ) was used for the analysis. The carrier gas was helium, with a 1-mL/min flow rate; the injector head pressure was 9 psi. The on-column injector temperature was 50°C, and the flame-ionization

detector temperature was 280°C. An injected volume of 1 μL was used. The oven temperature program is as follows: 45°C for 10 min, increased to 65°C at 1.5°C/min, increased to 190°C at 30°C/min, and held at 190°C for 10 min. The chromatographic separation is shown in Figure 1.

Coelution of BTEX and chlorobenzene with other hydrocarbons or additives present in gasoline was excluded by means of high-resolution gas chromatographic-mass spectrometric analysis.

Calibration

A 1- μL aliquot of each calibration solution (C₁-C₆) was injected, and the ratios between peak areas of each AH and ISTD were linearly related to the corresponding concentration ratios. Every calibration solution was injected five times, and the value of 0 was taken into account as the ultimate concentration level.

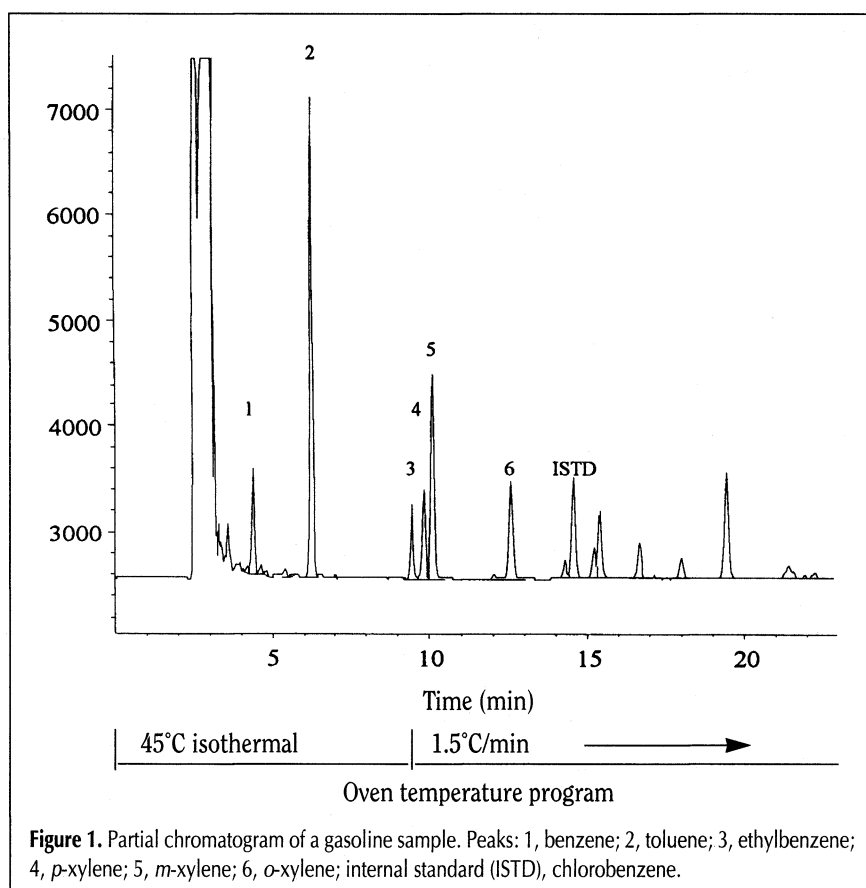


Figure 1. Partial chromatogram of a gasoline sample. Peaks: 1, benzene; 2, toluene; 3, ethylbenzene; 4, *p*-xylene; 5, *m*-xylene; 6, *o*-xylene; internal standard (ISTD), chlorobenzene.

Results and Discussion

Linearity

The correlation coefficient, standard error, slope (*b*), intercept (*a*), and the corresponding confidence limits ($p = .05$) for each AH are reported in Table II.

The linearity of the method was satisfactory. Furthermore, the intercept confidence interval ($a \pm \text{CL}$) includes the theoretical value of 0 for each compound, which confirms the very good correlation observed.

Precision and analysis of variance (ANOVA)

A single 1-L sample of gasoline was used to carry out the assessment of both reproducibility and accuracy. This test sample was stored at -18°C until the end of the experiment. Five aliquots of it were analyzed on different days according to the sample preparation procedure already described. Each sample was injected five times successively into the GC system. The sample mean and relative standard deviation were calculated for each compound (Table III).

These results were also submitted to a one-way ANOVA to evaluate the individual contribution of the variance components relative to the sample preparation step (σ_1^2) and instrumental measurement (σ_0^2). The within-sample mean square ($s^2 \text{ W-S}$) and the between-sample mean square ($s^2 \text{ B-S}$) were calculated (Table IV). The first ($s^2 \text{ W-S}$) depends exclusively on instrumental variation and it gives an estimate of σ_0^2 , whereas $s^2 \text{ B-S}$ is influenced by both sample preparation and instrumental variation and it

Table II. Linearity of the Method

Aromatic hydrocarbon	Correlation coefficient	Standard error	Slope	Intercept	Confidence limit (slope)	Confidence limit (intercept)
1	.999736	0.0233503	1.46597	0.00248952	0.03870	0.03129
2	.999595	0.116197	1.42923	0.00392540	0.04677	0.15573
3	.999330	0.0362507	1.42761	-0.00534352	0.06009	0.04858
4	.999240	0.0398825	1.49519	-0.00690055	0.06704	0.05341
5	.999336	0.0744051	1.46077	-0.0143646	0.06122	0.09972
6	.999174	0.0418453	1.46270	-0.00603799	0.06836	0.05608

gives an estimate of $\sigma_0^2 + n\sigma_1^2$, where n is the number of replicate measurements. Before the calculation of σ_1^2 was performed, a one-tailed F -test was carried out to assess whether s^2 B-S was significantly greater than s^2 W-S (i.e., whether σ_1^2 was significantly different from 0). For all of the compounds considered, the calculated F value was greater than the critical value of F tabulated at the 95% CL with 4 and 20 degrees of freedom ($F_{4,20} = 2.866$); hence, a significant difference was found. The σ_1^2 values, expressed as percentage of the total variation ($\sigma_0^2 + \sigma_1^2$), show that the variation due to the sample preparation step is lower than the contribution of the instrumental measurement for all the AHs considered, except for ethyl benzene, for which the contributions are roughly comparable.

Accuracy

Different amounts of a mixture of the AHs were added to

Table III. Sample Mean and Relative Standard Deviation (RSD) for Each Compound Considered

Aromatic hydrocarbon	Sample mean	RSD ($n = 5$)
1	1.20368	1.31
2	7.32059	0.95
3	1.54065	1.01
4	1.79109	1.03
5	4.34761	1.12
6	2.36520	1.03

Table IV. Precision Assessment Using Analysis of Variance and the F -test*

AH	S^2 B-S (4df)	S^2 W-S (20 df)	σ_1^2	σ_1^2 (%)	F
1	1.2384×10^{-3}	2.9443×10^{-4}	1.8879×10^{-4}	39.1	4.206
2	2.4311×10^{-2}	8.3064×10^{-3}	3.2009×10^{-3}	27.8	2.927
3	1.2026×10^{-3}	1.6530×10^{-4}	2.0746×10^{-4}	55.7	7.275
4	1.6920×10^{-3}	5.1773×10^{-4}	2.3485×10^{-4}	31.2	3.268
5	1.1800×10^{-2}	3.7452×10^{-3}	1.6110×10^{-3}	30.1	3.151
6	2.9889×10^{-3}	9.5921×10^{-4}	4.0594×10^{-4}	29.7	3.116

* Abbreviations: AH, aromatic hydrocarbons; S^2 B-S, between-sample mean square; S^2 W-S, within-sample mean square; σ_1^2 , variance component relative to the sample preparation step; F , variance ratio; df, degrees of freedom.

Table V. Accuracy Assessment

AH*	Calculated (%)			Measured mean (%) \pm SD* ($n = 5$)			Mean accuracy (%)		
	T ₁ *	T ₂ *	T ₃ *	T ₁	T ₂	T ₃	T ₁	T ₂	T ₃
1	1.57	2.20	2.49	1.50 ± 0.028	2.11 ± 0.022	2.39 ± 0.020	95.87	95.94	95.55
2	9.04	12.02	13.43	8.78 ± 0.070	11.74 ± 0.105	12.97 ± 0.134	97.20	97.69	96.63
3	1.88	2.46	2.74	1.80 ± 0.011	2.35 ± 0.025	2.59 ± 0.016	95.83	95.45	94.57
4	2.11	2.65	2.91	2.03 ± 0.022	2.55 ± 0.025	2.77 ± 0.015	96.20	96.02	95.34
5	5.63	7.81	8.85	5.37 ± 0.097	7.44 ± 0.090	8.33 ± 0.037	95.45	95.21	94.12
6	3.14	4.40	5.00	3.00 ± 0.026	4.14 ± 0.063	4.67 ± 0.055	95.51	94.03	93.50

* Abbreviations: AH, aromatic hydrocarbon; SD, standard deviation; T₁-T₃, three 1-g aliquots of the gasoline test sample.

three 1-g aliquots (exactly weighed) of the gasoline test sample. The aliquots (T₁-T₃) were submitted to the sample preparation step already described, then the final percent concentration of each AH was calculated by summing up the added amounts to the mean concentration of the test sample (Table III). Each sample was injected five times successively into the GC system. The mean percent ratio of the experimentally measured concentration to the calculated concentration (mean percent accuracy) was determined for each compound. In addition, the standard deviation of the five measurements of each sample was calculated. The results, summarized in Table V, show that a satisfactory degree of accuracy (93.50%–97.69%) achieved for all of the compounds at the various concentration levels.

Conclusions

This method for the determination of BTEX in gasoline shows an adequate degree of precision and accuracy and seems to be a valid alternative to the official procedures. Moreover, the quantitation of AHs with higher molecular weights present in gasoline, such as trimethylbenzene, ethyl toluene, and tetramethylbenzene isomers, can be achieved by means of simple modifications in the oven temperature program.

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