Fast-HRGC method for quantitative determination of benzene in gasoline

Ricardo R. Bonfim, Maria I.R. Alves, Nelson R. Antoniosi Filho *

Laboratório de Métodos de Extração e Separação (LAMES), Instituto de Química, Universidade Federal de Goiás, Campus Samambaia, C.P. 131, CEP 74001-970, Goiânia, GO, Brazil

HIGHLIGHTS
- The Fast-HRGC method allows chromatograph analysis of 8 min for gasoline.
- The method provides a good resolution between benzene and 1-methylcyclopentene.
- The method developed allows the quantification of benzene in gasoline.

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ABSTRACT
Gasoline is a very complex mixture of hundreds of different components and, from a toxicological point of view, benzene is the most hazardous one. Some of the methods recommended present many drawbacks, such as time-consuming. Thus, the need to develop fast methods for routine analysis of benzene is fundamental to the quality control of gasoline. Therefore, the present work compared two different capillary columns to develop a new method for routine analysis of benzene in gasoline by HRGC–FID. The quantitative analysis was carried out using external standard from 0.1%, 0.5%, 1.0%, 1.5% to 2.0% (v/v) of benzene in ethanol and in spiked gasoline. The results show that, using Fast-HRGC, it is possible to separate benzene and other 245 compounds found in gasoline in analysis time of 8 min with high accuracy.

1. Introduction
Gasoline is a complex mixture containing hundreds of compounds, mainly paraffinic, naphthenic, olefinic and aromatic hydrocarbons, with carbon numbers typically within the range from 4 to 12 [1,2].

Due to the new requirements in the quality control of fuels in recent years, the maximum tolerated concentration of some hydrocarbons has been limited, mainly aromatic and olefinic compounds, [3,4]. Among these, the reduction in the benzene level appears with prominence due to environmental reasons. From a toxicological point of view, benzene is an extremely hazardous component, once it is considered as a confirmed human carcinogen by several organizations, such as the International Agency Research of Cancer (IARC) and the American Conference of Governmental Industrial Hygienists (ACGIHs) [1,2,4–9]. The presence of benzene in the air is considerably attributed to motor vehicle exhausts [4]. Thus, in the last years, some countries have created laws to reduce and to regulate the levels of benzene in gasoline [2]. The countries of the European Community, USA, Japan and others have established in 1% (v/v) the maximum tolerated level of benzene in automotive gasoline [1–6].

In recent years, analytical techniques for benzene have been advanced significantly, and development continues. Modern technologies include gas chromatography (GC), comprehensive two-dimensional gas chromatography (GC×GC), high performance liquid chromatography (HPLC), mass spectrometry (MS), infrared (IR), ultraviolet (UV), and fluorescence spectroscopy, and combined techniques, such as GC–MS and GC–Fourier transform infrared (GC–FTIR). Among these techniques, capillary GC with flame ionization detection (FID) and capillary GC–MS are the most important and used for analysis of benzene in gasoline [1–3,10–13].

The selection of stationary liquid phase plays a vital role for achieving a particular separation in capillary columns. The stationary phases usually used for analysis of benzene in gasoline are polymethylsiloxane, TCEP [1,2,3-Tris(2-cyano ethoxy) propene] and cyanosilicones [1,3]. Pavlova and Ivanova [1] developed a method comparing two different capillary columns, PONA (polymethylsiloxane) and TCEP, for quantitative determination of benzene in gasoline by GC–FID. According to the authors, the success of GC–FID with the PONA column depends on the composition of the gasoline samples and it is not appropriate for routine analysis. Otherwise, GC–FID with a TCEP column enables precise and
accurate measurement of benzene content in gasoline, with different chemical composition, and with analysis time of 26 min.

The American Society for Testing and Materials (ASTMs) developed a series of test methods specifically for determination of benzene in gasoline by gas chromatography: ASTM Method D3606-10 [14] for determination of benzene and toluene in finished motor and aviation gasoline, but not applied to gasoline C. It has been mentioned that the method is not applicable to gasolines containing methanol; ASTM Method D5769-10 [15] describes the determination of benzene, toluene and total aromatics and total aromatics in finished gasolines. The method involves the analysis using capillary column for Fast-HRGC, however this method requires the use of deuterated internal standards that are extremely expensive; ASTM Method D5580-02 [16] describes the determination of benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9 and heavier aromatics in finished gasolines. This method presents a bad chromatographic profile, requires a pre-column and uses backflush systems, restricting its use and increasing the cost of the system.

Thus, the development of faster and simpler methods for routine analysis of benzene is fundamental to the quality control of gasoline. In these sense, shorter columns with reduced column diameter (0.15 mm ID, or less) have been used with growing popularity. In this way, these paper compared two different PONA capillary columns to develop a new faster method for routine analysis of benzene in gasoline by HRGC–FID.

2. Experimental

2.1. Reagents and standard solutions

Benzene and ethanol (both 99.5% purity) were acquired from Grupo Quimica Ltda and Belga Quimica Ltda, respectively.

2.2. Analytical curve

To external standard five calibration solution of benzene in ethanol were prepared using external standards from 0.1%, 0.5%, 1.0%, 1.5% to 2.0% (v/v).

To evaluate the effect of matrix a standard addition method was applied spiking a sample of gasoline with benzene in the following concentrations: 0.1%, 0.5%, 1.0%, 1.5% and 2.0% (v/v).

2.3. Samples

Gasoline standard sample was donated by REPLAN oil refinery (Brazil). Forty samples of automotive gasoline were collected from different gas stations such as Petrobrás, Shell, Texaco, Agip, Ipiranga, Esso, ALE and independent gas stations (“white flag”).

2.4. Chromatographic conditions

A GC Agilent 6890 Gas Chromatograph was used equipped with a split-splitless injector and a flame ionization detector (FID). The gasoline analysis was performed using two different columns. Both columns used hydrogen as carrier gas at 40 cm/s and nitrogen was used as make-up gas at 30 cm/s. In the HP-1 column, the injector

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**Fig. 1.** Chromatogram of gasoline showing the 1-methylcyclopentene and benzene peaks on HP-1 column for conventional HRGC.

**Fig. 2.** Mass spectra of 1-methylcyclopentene and benzene.
was operated in split mode with split ratio of 100:1 for a sample volume of 1.0 μL, and for DB-1 column, the injector was operated in split mode with split ratio of 300:1 for a sample volume of 0.2 μL. The injector and detector temperatures were 270 °C. All the chromatograms were acquired and processed using HP 3398A CG Chemstation data analysis software.

The first column was a HP-1 (60 m × 0.25 mm I.D. coated with a 1.0 μm film of polymethylsiloxane) for conventional HRGC. The oven was programmed as follows: 40 °C at 4 °C/min to 220 °C, with an initial isothermal period of 15 min at 40 °C. The total time analysis was of 60 min. The second column was a DB-1 (20 m × 0.10 mm I.D. coated with a 0.4 μm film of polymethylsiloxane) for Fast-HRGC. The oven was programmed as follows: 30 °C at 40 °C/min to 110 °C, and then to 200 °C at 15 °C/min. The total time of analysis was of 8 min.

3. Results and discussion

3.1. Development of methods

To develop a method for quantitative determination of benzene in automotive gasoline, it is necessary to achieve good chromatographic resolution of the benzene with regard to other compounds present in gasoline.

Initially, a method was developed using the conventional HP-1 column with 60 m of length. For this purpose, the experimental conditions – mainly oven temperature – were varied systematically to get the best possible chromatographic resolution using column HP-1 (Fig. 1). The HP-1 column presents a regular separation of benzene and 1-methylcyclopentene and a good chromatographic resolution for other compounds in automotive gasoline.

![Fig. 3. Chromatogram of gasoline showing the 1-methylcyclopentene and benzene peaks on DB-1 column for Fast-HRGC.](image)

![Fig. 4. Analytical curve of benzene quantification in gasoline. (A) Standard addition method; (B) External standardization method.](image)
sample. However, this column shows a long time-consuming (60 min) for routine analysis. Benzene and 1-methylcyclopentene were identified by HRGC–MS (Fig. 2).

The DB-1 column for Fast-HRGC allowed a better resolution between benzene and 1-methylcyclopentene than those obtained for HP-1 column for conventional HRGC (Fig. 3). The shorter length (20 m) and smaller internal diameter (0.10 mm) of the DB-1 column and the higher temperature rates used (40 °C/min and 15 °C/min) allowed a good resolution and faster analysis (8 min).

Thus, the Fast-HRGC method development using DB-1 column was used for quantitative determination of benzene in automotive gasoline samples purchased in gas stations in the city of Goiânia (Brazil).

3.2. Analytical curve

The Fig. 4 shows the analytical curve obtained by standard addition method (A) and the analytical curve obtained by external standardization (B), using Fast-HRGC column (DB-1). The analytical curves present a good correlation coefficient and the repeatability tests performed in gasoline sample showed coefficients of variation lower than 5% for each benzene concentration level.

The concentration of benzene in the same gasoline sample determined by the analytical curve A was 0.39 ± 0.00 (% v/v) and determined by the curve B was 0.37 ± 0.00 (% v/v). These results show that the effect of matrix is low.

3.3. Analysis of commercial samples

The content of benzene was determined in forty gasoline samples collected from different gas stations of the city of Goiânia (Brazil). Table 1 shows the results obtained for the analysis of the commercial gasoline samples. As it can be observed, the forty gasoline samples analyzed showed benzene amounts below the maximum level allowed by the Brazilian legislation, which is of 1% (v/v) [6].

Pavlova and Ivanova [1] have published that the success of GC–FID, with the PONA column with polymethylsiloxane as stationary phase for quantification determination of benzene in gasoline, depends on the composition of the gasoline samples and it is not appropriate for routine analysis. However, the present work showed that DB-1 column for Fast-HRGC enables precise and accurate measurement of benzene content in gasoline samples commercialized in Brazil. Therefore, the stationary phase is important in the chromatographic resolution, but the dimensions of the column are quite important as well.

Due to good chromatographic separation of benzene and others compounds, the method developed has the potential to be used in the evaluation of adulteration in quality control of gasoline, and used in the quantitative determination of toluene, methylbenzene, p/m-xylene, o-xylene (Fig. 5), C9 and heavier aromatics and total aromatics in gasoline.

4. Conclusions

This study developed a new and faster method for routine analysis of benzene in gasoline by Fast-HRGC.

Two different PONA capillary columns were compared to develop the method. The HP-1 column presented a regular resolution between benzene and 1-methylcyclopentene peaks and long time-consuming for routine analysis.

However, the DB-1 column for Fast-HRGC enabled the separation of benzene and 1-methylcyclopentene peaks and other 245 compounds present in gasoline in 8 min analysis. The Fast-HRGC method developed was applied in the accurate quantitative determination of benzene in Brazilian commercial samples of gasoline and, by these reasons, it was suggested the utilization of the Fast-HRGC method as an alternative to be used for internal quality control or screening purposes.

Table 1

<table>
<thead>
<tr>
<th>Gasoline sample</th>
<th>Benzene (% v/v)</th>
<th>Gasoline sample</th>
<th>Benzene (% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.52 ± 0.02</td>
<td>21</td>
<td>0.40 ± 0.01</td>
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<tr>
<td>2</td>
<td>0.44 ± 0.02</td>
<td>22</td>
<td>0.49 ± 0.02</td>
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<tr>
<td>3</td>
<td>0.48 ± 0.01</td>
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<td>0.60 ± 0.02</td>
</tr>
<tr>
<td>4</td>
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<td>0.35 ± 0.01</td>
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<td>6</td>
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<td>9</td>
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<td>10</td>
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<td>20</td>
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<td>40</td>
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</tr>
</tbody>
</table>

Fig. 5. Chromatogram of gasoline showing the separation of toluene, methylbenzene, p/m-xylene and o-xylene by Fast-HRGC.
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References