

Development and application of a chemical desorption method for determination of BTEX in ambient air from gas stations using gas chromatography

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ABSTRACT

Air pollution has caused damage to human health resulting from simple irritations and morbidity in the work to the development of cancer. An analytical method was developed to determination of benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene (BTEX) concentrations in samples of ambient air of gas stations by active sampling on adsorbent tubes containing activated charcoal followed by chemical desorption and analysis by gas chromatography with flame ionization detector. Tests were done using various solvents in order to verify the

recovery rate (RR) of each one of them. So, tests indicated that dichloromethane presented the best results of RR, with values above 75% of extraction of BTEX compounds. Sampling was performed in ambient air of gas stations located in Amargosa city in Bahia. The concentrations found in ambient air from gas stations ranged from 16.9 to 44.5 $\mu\text{g m}^{-3}$ for benzene; 39.9 to 247 $\mu\text{g m}^{-3}$ for toluene; 15.6 to 29.4 $\mu\text{g m}^{-3}$ for ethylbenzene; 12.7 to 68.5 $\mu\text{g m}^{-3}$ for m-xylene; 13.7 to 63.3 $\mu\text{g m}^{-3}$ for p-xylene and 13.0 to 42.2 $\mu\text{g m}^{-3}$ for o-xylene. The results obtained in this proposed method were compared with the results obtained in a comparative method using thermal desorption and showed no significant differences, confirming the validity of the method. The concentrations of the compounds found in this study are classified not carcinogenic to humans by RN (Regulatory Norm) - 15 from the Ministry of Labour and Employment in Brazil, with the exception of benzene.

Keywords: Air pollution, BTEX, Chemical desorption method, Occupational environments, Gas chromatography.

1 INTRODUCTION

The population growth in urban areas and the increasing number of vehicles in circulation have collaborated with unavoidable environmental impacts such as the pollution of water, soil and air. In recent years, it has grown the concern of the population about possible adverse health effects caused by exposure to air pollution, particularly in urban centers, where it is possible to notice the increase of the vehicle fleet and consumption of fossil fuels. This fact has contributed to the increase in emissions of air pollutants, aggravating environmental pollution and the health conditions of human beings. (SRIVASTAVA, 2006; RAS, 2010; MATYSIK et al., 2010; AMODIO et al., 2011; MAJUMDAR, 2011; ONGWANDEE et al., 2011; SUVARAPU, 2013, LANDRIGAN, 2017; GLENCROSS et al., 2020).)

The pollution in occupational environments has been also the focus of concern (GLINIANAIA et al., 2004; KAN et al., 2004; LERNER et al., 2012; KLINMALEE et al., 2009; BALTRÉNAS et al., 2011; SANJEL, 2016; NISHIDA; YATERA, 2022). Several diseases, such as allergies, irritations and various types of cancer have been reported in occupational environments, due to high levels of pollutants, especially those derived from petroleum through monoaromatic group constituted by benzene, toluene, ethylbenzene and xylenes - BTEX (DURMUSOGLU et al., 2010). In this group, benzene is considered by air monitoring agencies, both national and internationally (CONAMA, 2023; USEPA, 2023; EEA, 2023; WHO, 2023; OSHA, 2023; NIOSH, 2023), as a potential carcinogen to human being, while its derivatives have a lower toxicity, but with a high degree of risk to human health, especially when inhaled chronically (BALTRENAS et al., 2011).

Generally, BTEX compounds are found in the atmosphere of urban and industrial centers. Among the main sources of these compounds are industrial emissions and petroleum refining, handling solvents, vehicle emissions, distribution and storage of gasoline and losses due to fuel evaporation (BUCZYNSKA et al., 2009; KHODER, 2007; MACEDO et al., 2017; LATIF et al., 2019). However, the presence of BTEX compounds is not restricted to the urban and industrial centers, it occurs significantly in occupational environments, such as gas stations.

In recent years, several studies have been developed to determine the levels of pollutants in ambient air in urban areas, many of them are focused on the determination of BTEX compounds (MURENA, 2007; GALLEGO et al., 2008; ESTEVE-TURRILLAS et al., 2009; LIU et al., 2009; BAIMATOVA et al., 2016; HAMID et al., 2020). According to Dewulf and Langehoven (1999), most of the studies related to the BTEX analysis are currently focused on techniques for sampling and pre-concentration. After the sampling stage, the recovery of the analytes for analysis can be performed by thermal desorption (thermal volatilization with temperatures higher than the ambient), or solvent extraction. The preference for one of the techniques is strongly linked to the employed adsorbate/adsorbent agents (MEDEIROS et al., 2004). According to Namiesnik (1988), the technique of pre-concentration of volatile organic compounds on solid adsorbents have been applied since the 1970s and presenting some advantages, such as: simplicity, low cost, selectivity (using suitable adsorbent, mixed fills or tubes in series), the possibility of application in passive and active modes, quick analysis for thermal desorption coupled with gas chromatography.

Thermal desorption is a physical separation technique that uses heat to increase the volatility of contaminants that are removed from the solid matrix volatilized and shipped, usually directly to the chromatographic column for separation. It is typically applied for the determination of volatile organic compounds, vapors from synthetic materials or flavor compounds, food fragrances, etc. It is a high cost and destructive technique. The main advantages compared to using solvent extraction technique are the high sensitivity, low detection limits, eliminating the use of carbon disulfide (which is toxic and can cause interference in chromatographic peaks) and great potential for the automation of the injection process. Among the disadvantages are: the handling of the sample during extraction in offline mode, which can

cause contamination of the sample and the consumption of the entire sample in one analysis. However, as the entire sample is transferred to desorption occurs the increase of the sensitivity of the technique promoting the lowering of the detection limit and time of sampling (WOOLFENDEN, 1997; HALLAMA et al., 1998; BOEKER et al., 2010; OLKOWSKA, RATAJCZYK e WOLSKA, 2017; WOOLFENDEN, 2021).

The chemical desorption is used to remove strongly adsorbed analytes on activated carbon, which has a high retention factor and also catalytic activity. One problem with the use of activated carbon is that atmospheres with moderately high relative air humidity can absorb water carrying other analytes (MOON et al., 2001; GODOI et al., 2010). The extraction of analytes is usually made with solvents that have affinity with the retained analyte. For analysis of BTEX in the air using active or passive sampling, carbon disulfide (CS₂) is the most widely used solvent due to its high extraction capacity of the adsorbed molecules on activated carbon and also because it achieves better recovery efficiencies (NAJAFI et al., 2018).

In a study developed in 2010 in Poland to compare two types of passive samplers, the authors were able to extract, on average, 97% of BTEX compounds adsorbed on activated carbon using CS₂ as solvent (ZABIEGAŁA et al., 2010). Other advantage of CS₂ solvent is that it elutes quickly in the beginning of chromatogram and has a very low response of a flame ionization detector. Despite these advantages, the CS₂ is a highly toxic solvent (YAMASHITA et al., 1993; CHENG and NG, 1997; JOOS et al., 2003 and WANIA et al., 2003) reported on their studies, that the removal of organic compounds retained on solid adsorbents can be performed with other solvents such as methanol and dichloromethane. However, these solvents also present some toxicity.

The aim of this study was to develop an analytical procedure for collection BTEX at gas stations employing the chemical desorption with different solvents and GC-FID analysis. The sampling was conducted with personal collections near the region's breathing of the gas station attendant. Subsequently, the method was validated according to performance characterization suggested by IUPAC (2023) compared to the technique of thermal desorption. Finally, the method was used for the determination of BTEX compounds at gas stations in the city of Amargosa, Bahia.

2 MATERIALS AND METHODS

2.1 REAGENTS, SOLUTIONS AND SAMPLERS

Samplers tubes used to collect samples for chemical desorption analysis were SKC, 226-01 Series (70 mm long x 4 mm diameter) with 100 mg of activated carbon (20/40 mesh) in the analytical layer and 50 mg of activated carbon in the control layer. To collect samples for analysis by thermal desorption was used glass tube samplers Perkin Elmer (100 mm long and 6 mm diameter) containing one single section with 100 mg of activated carbon. The suction pump used for sampling was a SKC, AirChek model and the thermo-hygrometer used for temperature and humidity registrations was Incoterm, model 7663.

Benzene (99.9%), toluene (99.8%), ethyl benzene (99.5%), m-xylene (99.6%), p-xylene (99.9%) and o-xylene (99.5%) used for preparing the standard solutions were obtained from Merck (Germany) and Braskem (Brazil). The tested solvents to evaluate the chemical desorption of the analytes from tube samplers were: acetone (99.9%), ethanol (99.9%), methanol (99.8%), isopropanol (99.9%), n-hexane (99.2%), cyclohexane (99.9%), chloroform (99.4%) and dichloromethane (99.9%). All solvents were obtained from Merck.

Different stock solutions were prepared by diluting 100 μL of benzene and 1000 μL of other analytes in each tested solvent. To evaluate the recovery rate (RR) of the solvents, it was necessary to elaborate specific calibration curves for each of the BTEX compounds. The calibration curves of BTEX compounds were built from triplicate analysis of at least five known concentrations of analytes prepared by diluting the stock standard solution in the same solvent used in desorption. For benzene, concentrations of standard solutions varied from approximately 7 to 35 $\mu\text{g mL}^{-1}$, while for other analytes concentrations varied between 70-350 $\mu\text{g mL}^{-1}$.

2.2 EQUIPMENT AND ANALYSIS CONDITIONS

Determinations of BTEX after chemical desorption procedure were performed using a gas chromatograph with flame ionization detector, Varian model CP-3800. The analysis conditions were: injector 260 $^{\circ}\text{C}$; split mode: initial Split 50:1 and Split after 10 min 5:1. The initial oven temperature was 35 $^{\circ}\text{C}$ for 3.2 min; then increased from 35 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$ at a rate of 6.2 $^{\circ}\text{C min}^{-1}$ and on the last step increased from 60 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$ at a rate of 30 $^{\circ}\text{C min}^{-1}$, totaling 16.5 min run time. The detector temperature was 280 $^{\circ}\text{C}$. Two columns with different polarities were tested employing the same conditions described above. Initially it was tested a DB-1 capillary column (40 m x 0.20 μm x 0.100 mm) and then it was tested a comparative DB-Wax capillary column (30 m x 0.300 mm x 0.20 μm). The gases used on the chromatograph to perform the analysis were: synthetic air (flow rate 400 mL min^{-1}), hydrogen (flow rate 30 mL min^{-1}) and nitrogen in a flow rate of 30 mL min^{-1} . For the flow of the column (carrier gas) the hydrogen gas was used, with an average flow rate of 1.0 mL min^{-1} .

To determine the species of interest, such as comparative method, it was used an automatic thermal desorption (Model TurboMatrix ATD650, Brand Perkin Elmer, USA) coupled to a gas chromatograph with flame ionization detector. The analysis conditions of the thermal desorption were: transfer line temperature 50 $^{\circ}\text{C}$; desorption tube temperature 360 $^{\circ}\text{C}$; Trap desorption temperature 10 to 300 $^{\circ}\text{C}$ (99 $^{\circ}\text{C s}^{-1}$); Desorption flow 50 mL min^{-1} . The analysis conditions of the gas chromatograph were: initial oven temperature 40 $^{\circ}\text{C}$; After, it was increased from 40 $^{\circ}\text{C}$ to 120 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$ during a time of 5.0 min and finally, from 120 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$. The total run time was 16.5 minutes. The detector temperature was 250 $^{\circ}\text{C}$ and the capillary column used in the analysis was a PONA column with a stationary phase of methyl silicone (50 m x 0.15 mm x 0.50 μm). The gases and its flows used in chromatography were the same as described above in the analysis by chemical desorption.

2.3 CHEMICAL DESORPTION PROCEDURE FOR EVALUATION OF THE RECOVERY RATE

To the evaluation of the chemical recovery rate (RR) of analytes for each solvent studied, were injected in samplers tubes three aliquots with 4, 6 and 8 μL of stock solution containing the analytes, in duplicate, as suggested in the method 1501 by NIOSH (NIOSH, 2023). The tubes were sealed and then stored in a refrigerator overnight. For the process of desorption of BTEX compounds, the tubes were broken to remove the activated carbon contained in both analytical and control layer and they were transferred to different vials containing 1.0 mL of the investigated solvent for individual analysis. Then, the vials were sealed and shaken occasionally for 30 min to promote the desorption of adsorbed chemical compounds in the activated carbon, as suggested by NIOSH 1501 method. After the procedures for each desorption solvent aliquots of 1.0 μL of this solution containing BTEX compounds present within the solution were taken for chromatographic analysis. With the results obtained in the chromatographic analyses, was performed the calculations for determining the %RR for each solvent. The average of each solvent RR values were used for the correction of the mass of BTEX compounds for elucidate the final result.

2.4 CALCULATION OF THE CONCENTRATIONS OF BTEX COMPOUNDS

To determine concentrations of BTEX compounds in ambient air in gas stations using chemical desorption, it was first necessary to determine the total amount (M_a , in μg) of each analyte desorbed by the sum of the mass found in the analytical section adsorbent tube (M_c) and the mass found in the control section (M_b). After determining the total collected mass, corrections were made, depending on the RR of the studied solvent for calculating the real mass of each desorbed analyte (M_s). Finally, with the real value of the mass of each analyte, were performed the calculations to determine the concentrations, C , of the BTEX compounds, depending on the sampled air volume ($\mu\text{g m}^{-3}$, corrected to STP) (Equation 1).

$$C = \frac{M_s}{V \times RR} \times 1000 \quad \text{Equation 1}$$

To Godish (2004), the amount of collected analyte on adsorbent tubes should be directly proportional to the rate and duration of sampling to avoid sample losses by overloading or saturation of the adsorbent bed with the analyte sampled. Foley et al (2001) defined this volume as "breakthrough". In accordance with NIOSH 1501 method, if the mass (in μg) found in the control section of the adsorbent tube (M_b) is greater than 1/10 of the mass found in the analytical section (M_c), the method reports "breakthrough" and possible loss of the sample. In addition, possible interferences, such as alcohols, ketones and ethers are potential analytical interferences and may influence directly the rate of recovery of the analyte.

The analysis of BTEX compounds by the thermal desorption comparative method were conducted with the opening of the tube samplers and packaging on the thermal desorption with automated system. Calculations of concentrations, C, were performed according to the volume of air sample ($\mu\text{g m}^{-3}$, corrected to STP).

2.5 SAMPLING

The sampling of BTEX compounds was performed in air samples collected at resellers gas stations located in the city of Amargosa, Brazil. Amargosa is located in the Center-South of Bahia ($13^{\circ}01'48''$ S and $39^{\circ}36'18''$ W), and it has an area of 435.9 km² and a population of 37,557 inhabitants (IBGE, 2010). Sampling was conducted in five gas stations from different vendors, identified as S1, S2, S3, S4 and S5, which operate in two work shifts.

For the sampling, was used as reference the Method 1501 from Manual of Analytical Methods of the National Institute for Occupational Safety and Health - NIOSH (NIOSH, 2023). BTEX compounds were collected with the aid of a low flow vacuum suction pump, with flow meter and controller and a hose simultaneously connected to two collecting tubes of glass attached in his lapel, close to the breathing area of the attendant. These adsorbents tubes used in the sampling have their tips opened just at the time of collection, and they were coupled to the pump inlet air using an inert connector to a complete seal. The ambient air was collected during a workday (between 6 and 8 h), in a flow rate of 50 mL min⁻¹. During this step, sampling was performed using tubes for analysis by chemical desorption and thermal desorption. Sampling control (blank) was also performed at a point away from the areas of gas stations, and in the opposite direction of the winds coming from the analysed gas stations.

3 RESULTS AND DISCUSSION

3.1 EVALUATION OF THE RECOVERY RATE WITH DIFFERENT SOLVENTS

Considering that different mechanisms of sorption can occur between the BTEX compounds and activated carbon contained in all sampling, solvents with different polarities were selected to evaluate the extraction efficiency of each analyte. The solvents tested were: acetone, ethanol, methanol, isopropanol, n-hexane, cyclohexane, chloroform and dichloromethane. These tests were performed by applying the chromatography conditions described above and using DB-1 capillary column (40 m x 0.100 mm x 0.20 μm) because they exhibit better resolution and selectivity for the benzene compound. The results are shown in Table 1 as the average of the recovery rates of each analyte in the three tested concentrations levels.

Table 1. Average recovery rate (%) of BTEX compounds using different solvents in three distinct levels.

SOLVENTS	Analyte					
	Benzene	Toluene	Ethylbenzene	m-Xylene	p-Xylene	o-Xylene
Acetone	51,23 ± 0,02	38,03 ± 0,01	47,70 ± 0,01	23,57 ± 0,07	20,63 ± 0,04	14,43 ± 0,01
Ethanol	30,21 ± 0,02	32,15 ± 0,01	25,98 ± 0,03	12,03 ± 0,01	7,35 ± 0,01	5,12 ± 0,01
Methanol	25,13 ± 0,04	13,73 ± 0,01	14,40 ± 0,01	8,37 ± 0,01	6,20 ± 0,01	5,67 ± 0,01
Isopropanol	16,47 ± 0,01	13,57 ± 0,01	16,17 ± 0,02	12,70 ± 0,03	5,00 ± 0,01	5,67 ± 0,01
Chloroform	67,77 ± 0,06	67,57 ± 0,05	87,13 ± 0,03	64,23 ± 0,04	59,27 ± 0,04	46,73 ± 0,04
Dichloromethane	84,03 ± 0,02	79,50 ± 0,01	91,00 ± 0,01	77,57 ± 0,01	75,77 ± 0,01	76,00 ± 0,02
n-Hexane	33,70 ± 0,07	33,83 ± 0,06	53,27 ± 0,05	30,30 ± 0,04	27,53 ± 0,05	17,23 ± 0,03
Cyclohexane	17,43 ± 0,01	10,00 ± 0,01	13,30 ± 0,003	6,37 ± 0,01	6,03 ± 0,02	4,33 ± 0,002

From the results shown in Table 1, it can be noticed that when more polar solvents are used, such as ethanol, methanol and isopropanol, the RR did not exceed 32%. Low recovery rates were also observed when non-polar solvents such as n-hexane or cyclohexane were used. For cyclohexane, the related RR was between 4 and 17%, while for n-hexane, the RR were between 17 and 53%. However, it can be seen that with the use of solvents with intermediate polarity, such as dichloromethane and chloroform, the recovery rates of BTEX compounds was higher, and the best results were found when using dichloromethane, resulting in a RR greater than 75% for all analytes.

According to Helffrich (1962), the activated carbon is considered a natural ion exchanger, with this property being enriched by chemical activation. The carbon surface has a layer of delocalized π electrons that can be distorted and generate positive and negative temporary electrons densities that can attract free ions in solution or suspension. As BTEX compounds have similar characteristics to activated carbon (as like the presence of aromatic ring, for example), they are efficiently retained in by this holder. In the case of dichloromethane, which has medium polarity, it is possible that it works isolating the π clouds of the molecules of BTEX compounds and the surface of the carbon, disfavoring its distortions. Therefore, desorption is more efficient with dichloromethane.

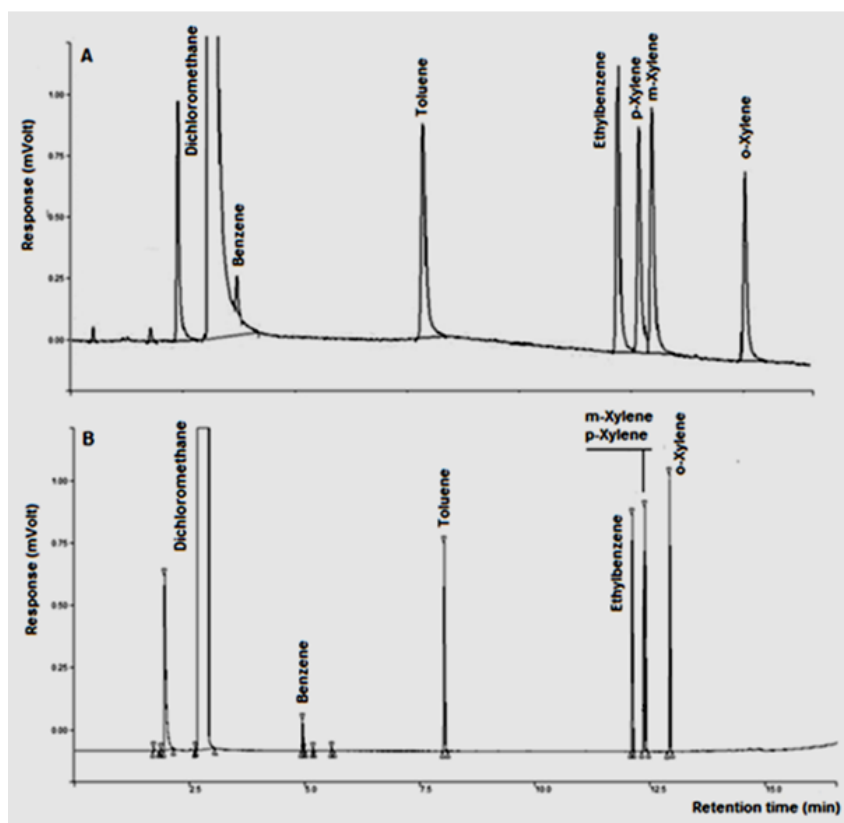
The 1501 NIOSH method for determining BTEX in the air recommends that the solvent must present a recovery rate equivalent or higher than 75% for the method to be considered appropriate. Among the studied solvents, dichloromethane showed the best results within established by the proposed method. Furthermore, it is necessary to consider that when compared with carbon disulfide (which is the recommended solvent by the 1501 NIOSH), dichloromethane is less toxic and can be easily handle. Therefore, dichloromethane was selected as alternative solvent extractor to carbon disulfide for determination of BTEX in ambient air in gas stations.

3.2 SELECTION OF THE CHROMATOGRAPHIC COLUMN

Once selected the solvent extractor, the evaluation of the separation of BTEX compounds was performed by comparison of two chromatographic columns with different polarities. The operating conditions of the chromatograph were the same for both tests and were based on 1501 NIOSH method.

Initially, it was checked the separation of analytes using a DB-1 capillary column with a non-polar stationary phase of dimethylpolysiloxane and then with a comparative DB-Wax column, with a polar stationary phase with polyethylene glycol. In both columns, appropriate separations of analytes were obtained (Fig. 1).

Fig. 1. (A) Chromatogram of BTEX compounds using DB-Wax chromatographic capillary column (30 m x 0.300 mm x 0.20 μm); (B) Chromatogram of BTEX compounds using DB-1 capillary column chromatography (40 m x 0.100 mm x 0.20 μm). Chromatographic conditions: Injector temperature 260 $^{\circ}\text{C}$; Initial split 50:1 and split after 10 min. 5:1; The oven temperature of GC was initially held at 35 $^{\circ}\text{C}$ for 3.2 min, raised to 60 $^{\circ}\text{C}$ at a rate of 6.2 $^{\circ}\text{C min}^{-1}$ and then raised to 220 $^{\circ}\text{C}$ at a rate of 30 $^{\circ}\text{C min}^{-1}$.



In the column with polyethylene glycol phase (chromatogram A), the separation of xylenes was more effectively, however the elution of benzene was occurring very close to the solvent. Moreover, the column with dimethylpolysiloxane phase (chromatogram B), the peak referred to benzene was obtained with adequate selectivity and even the peaks related to meta-xylene and para-xylene being close, the integration and quantification of these compounds was possible. Thus, the chromatographic column with dimethylpolysiloxane stationary phase was selected for subsequent tests.

3.3 ANALYTICAL PARAMETERS

The concentrations of analytes for the construction of calibration curves were established based on BTEX concentrations recommended by 1501 NIOSH method. Thus, for benzene concentrations of standard solutions vary from approximately 7 to 35 mg mL^{-1} , while for other analyte concentrations ranged 70 to 350 $\mu\text{g mL}^{-1}$. Table 2 shows the calibration curves for each analyte, and the coefficients of determination

(R2). As can be noticed, the values of R2 for all analytes were above 0.99, which confirms that the calibration curve of the proposed method has adequate linearity for the proposed work.

Table 2. Validation parameters for the analysis of BTEX compounds by chemical desorption method using dichloromethane as solvent.

Compounds	DL ($\mu\text{g m}^{-3}$)	QL ($\mu\text{g m}^{-3}$)	Calibration Curves	R ²	RSD Repe. (%)	RSD Repro. (%)
Benzene	5,54	16,78	$y = 0,0962 x - 1,2140$	0,9924	2,95	3,79
Toluene	15,05	45,54	$y = 0,1050 x - 15,924$	0,9916	4,24	5,02
Ethylbenzene	15,50	46,93	$y = 0,1040 x - 14,140$	0,9920	4,59	5,03
m-Xylene	11,29	34,26	$y = 0,1014 x - 15,661$	0,9924	4,61	5,09
p-Xylene	13,56	41,09	$y = 0,1011 x - 12,090$	0,9934	4,64	5,07
o-Xylene	12,87	39,06	$y = 0,1013 x - 12,861$	0,9940	4,66	5,13

DL = Detection Limit; QL = Quantification Limit; RSD Repe. = Relative standard deviation of repeatability; RSD Repro. = Relative standard deviation of reproducibility; Intradays accuracy tests were conducted with five different analysts; Calibration Curve: y = Concentration of analyte and x = Chromatographic peak area

Precision was evaluated by repeatability and intermediate precision studies (interday precision) by evaluation of tests developed in five different analysts in different days (RIBANI et al., 2004). The repeatability tests for BTEX compounds revealed coefficients of variance between 3.0 and 4.5%. The intermediate precision tests indicated that the values of relative standard deviations (RSD%) were 5.0% (Table 2). The statistical analysis of the data showed no significant differences between the analyses performed in different periods by different operators, indicating that the method is appropriate to repeatability tests and also to interday precision tests developed by the different analysts.

To evaluate the accuracy of the method was performed addition and recovery tests, with varied concentrations of the analytes from 21 to 211 $\mu\text{g mL}^{-1}$. In test, 10 samples were analysed and the noticed recoveries values were between 97.5 and 99.5 %. The applicability and validation of the method was verified by comparing the results obtained by the proposed method with chemical desorption results of a comparative thermal desorption method using the same sampling conditions. The validity of the method was verified statistically by paired t-Student test. With the obtained result for 6 degrees of freedom by the t-Student test was $T(6;0,025) = 0.7554 \ll t = 2.776$, and with 95% degree of confidence it is possible to confirm that the results of the analyses of both methods did not differ significantly. Thus, the concentrations of BTEX compounds found in gas stations in the city of Amargosa, Bahia, had concentrations in the same order in two methods.

The detection limit (DL) and the quantification limit (QL) were determined based on parameters of the analytical curve. The DL and QL are expressed according to Equations 2 and 3:

$$DL = \frac{3,3s}{b} \quad \text{Equation 2}$$

$$QL = \frac{10s}{b} \quad \text{Equation 3}$$

Where s indicates the standard deviation of responses and b is the slope of the calibration curve. The estimated s was obtained by the values of interception of the line on the y -axis for different calibration lines (ICH, 2022). Table 2 shows the values obtained for DL and QL of the studied BTEX compounds. The related DL and QL values in this study were higher than the findings in the scientific literature for the determination of BTEX compounds (WANG and ZHAO, 2008; LIU et al., 2009; LLOP, 2010; NICOARA, 2010; CORREA et al., 2012) and showed lower sensitivity compared to DL and QL values of the comparative method of thermal desorption, however, the values were suitable for the detection of these compounds at gas stations because the findings were smaller than the tolerances limits recommended by national and international regulators agencies (MTE, 2023; NIOSH, 2023; OSHA, 2023).

3.4 APPLICATION OF THE METHOD TO REAL SAMPLES

The method was applied to the determination of BTEX in ambient air samples collected from five gas stations (Stations 1-5). The results obtained after desorption of analytes from tube sampler using dichloromethane as eluent, as well as employing thermal desorption as a comparative procedure are shown in Table 3. There were no related mass losses by "breakthrough" because there were no detected quantities of BTEX compounds in the control sections of the adsorbent tubes. For both procedures, the higher concentrations of BTEX compounds were found at Station 3 and the minimum levels at Station 1. Control tests (blank) were conducted in a remote area, far from the region of the gas stations, and presented undetectable concentrations for all analytes. Among the tested compounds, toluene was the compound that showed the highest concentrations (39.9 a 247 $\mu\text{g m}^{-3}$) for chemical desorption method.

The levels of toluene, ethylbenzene and m,p,o-xylenes related in all gas stations were lower than the maximum limits recommended by NIOSH (NIOSH, 2023), and by the NR-15 of Brazilian Ministry of Labour and Employment (MTE, 2023). However, a study conducted by the World Health Organization (WHO, 2023), benzene is demonstrably carcinogenic to humans. The WHO estimates that exposure to 1.0 $\mu\text{g m}^{-3}$ of benzene during a period of 15 years causes the addition of approximately 6 cases of leukemia per 1,000,000 inhabitants. BTEX intoxication, especially with benzene, is slow and cumulative, as these pollutants are slowly metabolised and excreted from the body.

Table 3. Concentration of BTEX ($\mu\text{g m}^{-3}$) in ambient air from gas stations located in Amargosa, Bahia, after chemical desorption procedure of analytes using dichloromethane (A) and by thermal desorption (B).

Sampling Location	Benzene	Toluene	Ethylbenzene	m-Xylene	p-Xylene	o-Xylene
				(m + p-Xylenes)		
Station 1						
A	16,9	49,5	16,3	12,7	13,7	13,1
B	14,8	59,4	10,4	(29,6)		11,4
Station 2						
A	28,5	39,9	15,6	13,6	14,0	13,3
B	31,9	42,5	10,6	(31,8)		15,9
Station 3						
A	44,5	247	29,4	68,5	63,3	42,2
B	37,4	262	37,4	(123,0)		42,8
Station 4						
A	17,6	43,1	15,8	20,8	19,4	13,0
B	12,3	49,2	13,3	(29,5)		14,7
Station 5						
A	17,2	151	15,9	31,0	25,4	26,7
B	14,5	149	19,3	(57,8)		24,2

3.5 COMPARISON OF RESULTS FROM OTHER RESEARCH PAPERS

When the results of this study are compared with studies conducted in other Brazilian cities and cities around the world (Table 4), the finding levels are comparable to related values in studies developed in Brazilian cities such as Rio de Janeiro, Porto Alegre and São Paulo and in some Asian cities such as Ho Chi Minh (Vietnam), Calcutta (India), Rome (Italy) and Cairo (Egypt). The toluene concentration levels found are the highest in all studies.

It is noteworthy that most of the samples taken in these studies took place in diverse environments, such as highways, homes, schools, buses, cars, trains, commercial areas, airports, rural areas, offices, shopping malls and others. In the study of gas stations in Rio de Janeiro (CORREA et al., 2012), it was noticed that the results obtained are close to the results obtained in this work, except for the levels of toluene that, in this present study, had a mean of $106.2 \mu\text{g m}^{-3}$ and the levels in Rio de Janeiro were $47.7 \mu\text{g m}^{-3}$. BTEX levels occurred almost in the same concentrations. The levels found in Cairo, Egypt, generally were the highest ones, with average concentrations of 87.2; 213.8; 43.3; 140.8 and $73.8 \mu\text{g m}^{-3}$ for the BTEX compounds respectively, and the levels of meta and para-xylene were determined as a single level.

Table 4. Comparison of levels of BTEX ($\mu\text{g m}^{-3}$) among different cities.

City/Country	Benzene	Toluene	Ethylbenzene	m-Xylene (m-p-Xylene)	p-Xylene	o-Xylene	Sampling location	References
Amargosa / Brazil	24,9	106,1	18,6	29,3	27,2	21,7	Gas stations/Urban Area	This Work
Rio de Janeiro / Brazil	29,7	47,7	23,3	(46,9)		14,3	Gas stations/Urban Area	[MARTINS et al., 2007]
Porto Alegre / Brazil	24,9	43,1	13,7	(28,0)		11,0	Traffic road/Urban Area	[GROSJEAN et al., 1999]
São Paulo / Brazil	4,8	45,1	15,6	(30,7)		7,8	Traffic road, Park, Airport, Commercial area/Urban Area	[COLÓN et al., 2001]
Hochiminh / Vietnam	56,0	121,0	21,0	(64,0)		23,0	Traffic road/Urban Area	[LAN AND MINH, 2013]
Kolkata / India	29,2	45,4	13,1	(32,9)		11,9	Commercial area, Residential area, Industrial area/Urban Area	[MAJUMDAR et al., 2011]
Rome / Italy	35,5	99,7	17,6	(54,6)		25,1	Traffic road/Urban Area	[BROCCO et al., 1997]
Cairo / Egypt	87,2	213,8	43,3	(140,8)		73,8	Traffic Road/Urban Area/Rural Area	[KHODER, 2007]
Birmingham / England	7,3	15,1	1,6	(5,2)		1,4	Commercial area, Residential area/ Urban Area	[KIM et al., 2001]
Santiago / Chile	14,8	29,8	6,5	(25,2)		8,9	Traffic road/Urban Area	[GEE and SOLLARS, 1998]
Hamburg / Germany	1,4	4,7	ND*	(0,88)		ND	Residential area/Urban area	[SCHNEIDER et al., 2001]
Hong-kong / China	4,85	28,8	3,11	(3,98)		2,85	Traffic road/Urban Area	[HO, 2002]
Delhi / India	60,22	162,68	49,42		25,25*		Traffic road/Urban Area	[GAUR et al., 2016]
Ardabil / Iran	32,40	16,10	62,38		13,82*		Beauty Salons/Urban Area	[BAGHANI et al., 2018]
Klang Valley/Malasya	25,82	89,08	23,89	37,25		35,80	Traffic road/Urban Area	[FANDI et al., 2020]

*Sum of m-p-o-Xylene compounds.

4 CONCLUSION

The chemical desorption method proposed in this paper, using dichloromethane replacing carbon disulfide, allowed simultaneously identify and quantify the presence of BTEX compounds in ambient air from gas stations. The chromatographic method was validated, exhibiting accuracy, precision and suitable limits of detection and quantification for studies with ambient air. The chemical desorption proposed method was compared to thermal desorption method, obtaining consistent results, demonstrating that the use of chemical desorption to determine the BTEX compounds using dichloromethane as solvent can be employed alternatively, as its toxicity, handling and cost are more appropriate than carbon disulfide. Concentrations of BTEX showed how the gas stations are potentially insalubrious places, especially considering exposure to benzene, what is more dangerous to workers in these locations. Importantly, the results obtained along this study should be viewed as indicative and not as conclusive, since it is essential that more monitoring should be drawn for definitive conclusions.

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