BTEX COMPOUNDS EVALUATION USING CERTIFIED REFERENCE MATERIAL AND SPIKED SAMPLING TUBE

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Abstract: In order to corroborate the efficiency of PET bottle inspection equipment coupled with mass spectrometry detection, a method for determination of BTEX presented in the interior of returnable PET bottles was developed and validated. It was verified that the method was able to detect BTEX compounds in the range 0.1-10mL of gasoline.

Key words: BTEX, PET bottle, activated charcoal tube.

1. INTRODUCTION

By the late 80´s, a disposable bottle made of **Polyethylene Terephthalate** - or PET, appeared as a light and cheap option to substitute the heavy and high maintenance glass bottles. Unfortunately, at that moment, it was not a concern a destiny for the entire PET bottle produced. Brazil produces about 3 billion bottles PET annually, a product 100% recyclable, but the recycling volume is currently only 50%[1]. A solution to minimize the environmental impact seems to be returning and reusing the same bottles, or even recycling them. However, the big fear with refillable PET is that these containers can be contaminated by using as holding vessels for cleaning chemicals, petroleum products (crude oil, diesel fuel and gasoline) and pesticides[3].

Benzene, toluene, ethylbenzene and xylenes (BTEX) are the chemical markers to indicate the contamination from petroleum products[4]. Acute exposures to high levels of gasoline and its BTEX compounds have been associated with skin and sensory irritation, central nervous system depression, and effects on the respiratory system[5-8]. In such case, small amounts of these substances can affect the taste and safety of beverages. Hence, in order to assure that refillable PET bottles are out of toxic contaminants, beverage industries have been using an inspection equipment to detect contaminated bottles.

2. PURPOSE

The aim of the work was to demonstrate the validation of analytical method for the determination of BTEX in sampling tubes with activated charcoal and apply the proposed procedure to compare the results of PET bottles contaminated with gasoline from the contamination detection system.

3. METHODS

3.1. Contamination detection system sampling and analysis procedure

The contamination detection system (CDS) is a device installed directly on a single-lane conveyor which transport empty PET bottles before the cleaning step. The analysis procedure begins with the injection of 150mL of an inert gas into the bottle while a vacuum pump system takes a gas sample as the bottles pass by. The collected sample is ionized and goes through to a quadrupole mass spectrometer and routed through an electromagnetic fields to detector. There, the substance is sequentially broken down by molecule mass in order to quantify the various masses. If any of the bottles analyzed by CDS presents a toxic substance, it is sorted out of the conveyor to eliminate the possibility of refilling a contaminated bottle.

3.2. Laboratory sampling and analysis procedure

The NIOSH (National Institute of Occupational Safety Healthy) 1501[9] was modified to be the method used to collect the volatile organic compounds present inside the bottles.

A sampling tube with 100/50mg of activated charcoal as adsorbent (SKC Sorbent Tube 226-01, Anasorb CSC, Coconut Charcoal, 6 X 70 mm size, 2-section, with GS ends, FFW separators) was placed in the entrance of the bottle. The sampling tube was coupled to a vacuum pump system to promote the gas sample withdrawing. In order to simulate the sniffer procedure, it was taken the same amount of gas that is sampled by the contamination detection system (150mL). After sampling, the tube was broken and the charcoal adsorbent was transferred into a 2.0 mL vial, where BTEX was extracted using 1mL of carbon disulfide within 30 minute ultrasonic bath. Thermo Electron model Focus GC / DSQ gas chromatograph coupled to a mass spectrometer was employed for experimental analysis in this study. A DB-624 (6% Cyanopropyl-phenyl + 94% dimethyl polysiloxane) capillary column, 60 m length x 0.32 mm, 1.8µm film thickness was chosen for separation of BTEX compounds. Capillary column flow of pure He carrier gas was set at 2.0 ml/min. The injector was set at 220°C and the 1uL injection was done in the split mode (1:20 split ratio). Oven temperature was initially programmed at 50°C for 6 minutes and temperature was increased at the rate of 20°C/min to 80°C and after 2 minutes, in order to cleanse the column from residual BTEX compounds, the temperature was increased to 170°C in a rate of 20°C/min and held constant for 3 minutes. The GC/MS interface line and the ion source were maintained at 250°C and 200°C, respectively. Electron energy was 70eV and electron emission 100µA.

4. RESULTS AND DISCUSSION

4. 1. Validation Method

Selectivity, linearity, precision (repeatability and intermediate precision), accuracy and limits of detection and quantification parameters were studied, according with the guidelines of the document INMETRO (Brazilian Metrological Institute) DOQCGCRE-008[10]. The chromatogram of the extract of a spiked charcoal activated tube showed no inferring peaks at retention times of BTEX compounds. All the calibration curves presented a correlation coefficient above 0.99. Limits of detection and quantitation were calculated from the response of the lowest standard concentration of each compound spiked in 10 activated charcoal tubes (table 1). The relative standard deviations obtained for the repeatability at different spiked levels of BTEX compounds are bellow 10% and the intermediate precision comparing two different devices (GC-MS) sowed values for F and T tests bellow than table values. Therefore, the precision of this method seams to be acceptable.

A certified reference material of sampling tube with activated charcoal containing benzene, toluene, o-xylene and m-xylene (BCR-562, Institute of Reference Materials and Methods – IRMM, Belgium) was used to evaluate the accuracy of the method. In the case of ethylbenzene was used a spiked blank sampling tube. As depicted in the table 1, the accuracy study demonstrated a recovery range between 92-112%.

Table 1. Recoveries studies of BTEX compounds using CRM and spiked sampling tube

Analyte	CRM (µg)	Spiked tube (µg)	RSD (%)	Recovery (%)	Confidence Interval (+/-)	LD (µg)	LQ (µg)
Benzene	15.0	**	7.5	97.1	4.0	0.2	0.5
Toluene	147.0	**	6.5	91.6	3.0	1.2	3.8
Ethyl benzene	**	25.0	4.0	99.8	2.0	1.2	4.0
o-Xylene	93.0	**	4.8	112.2	4.0	2.3	7.5
m-Xylene	96.4	**	5.1	109.2	2.0	2.4	8.1

4.2. Uncertainty

The uncertainty determination for BTEX analysis was evaluated based on the Guide to the Expression of Uncertainty in Measurement and on the ISO GUM. The values of measurement uncertainty were expressed in terms of expanded uncertainty (U), which was determined by multiplying the coverage factor by the combined standard uncertainty of the input quantity.

The greater contributions come from the uncertainty of repeatability and analytes purity (Figure 1).

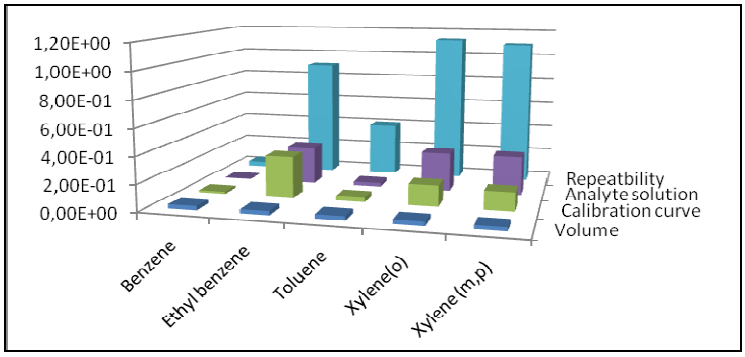

Fig.1. Uncertainty sources contributions

4.3. Comparison Between Contamination Detection System (CDS) and the Validated Method

The content of six bottles with different amounts of gasoline were analyzed by Contamination Detection System and by the validated method. The results (table 2) indicated that the validated method was able to identify and quantify all the BTEX compounds presented in contaminated bottle with 10mL of gasoline. In the bottles with 5mL of gasoline only benzene and toluene were quantified. However, all the BTEX compounds presented in contaminated bottles with 0.1mL of gasoline were identified.

5. CONCLUSION

The analytical method developed to analyze BTEX compounds from charcoal tubes complied with the validation parameters: linearity, LOD, LOQ, repeatability, intermediate precision, accuracy/recovery and uncertainty.

Validated method is efficient to identify BTEX contaminants presented in refillable PET bottles in very small amount of gasoline (0.1mL). However, only contaminated bottles with amounts above 5mL of gasoline presented all the BTEX compounds quantified.

In order to improve method sensitivity, we suggest collecting higher volumes of air from the inside of the bottles. NIOSH 1501 showed that BTEX compounds can be sampled in volumes much higher than the 150mL used in the sampling step.

Table 2. Study of comparision sensitivity between CDS and the validated method with known contaminant (gasoline)

Bottle	Contaminant (gasoline)	Validated Method				
		Benzene (ppm)	Toluene (ppm)	Ethyl Benzene (ppm)	(o)Xylene (ppm)	(m,p)Xylenes (ppm)
1	none	N.D.*	N.D.*	N.D.*	N.D.*	N.D.*
2	10mL	105.2	159.3	27.3	38.0ppm	51.4ppm
3	5mL	59.5	48.9	≥ LOQ (14ppm)**	≥ LOQ (13ppm)**	≥LOQ (17ppm)**
4	5mL	44.6	47.9	≥LOQ (10ppm)**	≥LOD	≥LOQ (12ppm)**
5	0.1mL	≥ LOD	≥ LOD	≥ LOD	≥ LOD	≥LOD
6	0.1mL	≥ LOD	≥ LOD	≥ LOD	≥ LOD	≥ LOD
7	0.1mL	≥ LOD	≥ LOD	≥ LOD	≤ LOD	≤ LOD

*N.D. – Not detected

**The values in the brackets were estimated, since those values were below the first concentration level of the calibration curve.

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