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(RECOMMENDED CITATION)

INDOOR AIR BTEX MEASUREMENTS

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ABSTRACT. An improved quantitative method was used for measuring benzene, toluene, ethyl benzene, *m*/*p*-xylene and *o*-xylene (BTEX)] by preconcentration on active charcoal followed by gas chromatography-mass spectrometry (GC/MS) analysis. The selected ion monitoring (SIM) mode was used for the quantitative GC/MS analysis. The internal standard used was stable isotopically labeled benzene. The compounds of interest were eluted in 7.5 min. The method is simple, rapid and shows good validation parameters (linearity, precision and accuracy) for the studied compounds. The method was tested for the investigation of the indoor emissions from different materials and furniture. The results showed that attention should be paid to the new furniture and to the inflating indoor of the new vacuum packed mattresses.

Keywords: *GC/MS, BTEX, isotopic dilution, SIM*

INTRODUCTION

Benzene, toluene, ethyl benzene and xylene (BTEX) are widespread pollutants having as main sources the vehicle traffic in the outside environment and the cigarette smoke in the indoor environment. They are also present in small quantities in drinking water and food, in painting substances or adhesives. The high toxicity of aromatic hydrocarbons, especially of BTEX, present in gasoline, paint thinner, glue and adhesive products and used as solvent, is well known. The chronic exposure to benzene and other aromatics, followed by their vapor inhalation, could cause disorders in the central nervous system and gastrointestinal tract, but the most relevant consequences of chronic poisoning are anemia and leukemia [1, 2]. The effects of indoor air pollution on human health are of high concern. The minimal risk level (MRL) is estimated for the human exposure/day to a hazardous substance that is without appreciable risk of adverse non-cancer health effects over a specified

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duration of exposure [3]. Environmental Protection Agency estimated that 13 - 45 µg m^{-3} BTEX in air may be responsible for developing cancer [4, 5]. The outdoor maximum limit recommended for benzene by the European Community is 10 $\mu g \cdot m^{-3}$ [6]. Occupational maximum exposure limit is 16 $mg \cdot m^{-3}$ [7]. A major class of contaminants of indoor air, the volatile organic compounds (VOCs), may be up to 10 times higher indoors than outdoors. This indicates contributions from indoor sources such as furniture wax, smoking, paints, glues, carpets and also breathing or body odor. These chemical mixtures are recognized as causative agents of “building-related illness” or “sick-building syndrome” [8]. The methods used for volatile organic compounds sampling presume preconcentration of samples on adsorbents. All the methods vary from each other according to the sampling technique, type of sorbent, method of extraction and detection technique [9, 10]. BTEX have been considered as hazardous by the amendments of 1990 in the Clean Air Act (USEPA 1990). Benzene was classified as human carcinogen of Group A [11]. Since most people spend almost 90% of their time inside a building, indoor air pollution is a significant concern. Recent data indicate that asthma and allergies in children are most pronounced in the developed countries [12].

Gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) are the most used quantitative methods for VOCs levels determination in the air [1-30].

The aim of the present work was to improve and apply a GC/MS method to evaluate the toxic aromatic ambient pollutants. The internal standard used was stable isotopically labelled benzene. The GC/MS method was used in the selected ion monitoring (SIM) mode for determining the levels of indoor air BTEX concentrations.

RESULTS AND DISCUSSION

The GC/MS method developed for BTEX determinations in indoor air is simple and rapid. The mass spectrometer operating in the SIM mode gave a high selectivity and specificity to the method developed, which allowed the peak deconvolution of benzene and its deuterated analogue internal standard, as they were co-eluting in the total ion chromatogram. Also SIM mode offers higher sensitivity than the scan mode. The validation of the method gave good values for precision, R.S.D. of 3.02 – 18.75 % and accuracy, between 0.59 - 17.8% in the case of deuterated benzene used as internal standard in comparison with the case of using pyridine as internal standard, when precision was lower than 25.8%, and accuracy was lower than 24.9% [24]. The limit of detection for BTEX was of 0.01µg. By using active charcoal cartridges for BTEX determination, the extraction method is rapid and inexpensive.

The linearity parameters obtained for BTEX in the range 0 – 80 µg by using deuterated benzene as internal standard are presented in Table 1 and Fig.1 in comparison with BTEX linearity parameters obtained for BTEX in the range 1-100 µg by using pyridine as internal standard. Very good coefficients of regression were obtained for deuterated benzene internal standard (r > 0.99) in comparison with those obtained with pyridine as internal standard (r>0.90). Precision, calculated by using deuterated benzene as internal standard for the aliquot samples of 40 and 80 µg, showed R.S.D. values between 13.13 – 18.75 % and respectively between 3.02 - 6.41%. The accuracy R.S.D. calculated values were between 2.5 - 17.7 % for the sample of 40 µg and between 0.59 - 17.8 % for the sample of 80 µg. In the case of using pyridine as internal standard, precision and accuracy were lower than 25.8%, respectively 24.9% [24].

Table1. Linearity for BTEX

Range: 0-80µg (IS: 1mg deuterated benzene)		
Compound	Regression curve	r
B	y=0.0017x+0.0032	0.997
T	y=0.0032x+0.0188	0.988
E	y=0.0029x+0.0067	0.996
X	y=0.0065x+0.0139	0.997
Range: 0- 100µg (IS: 1mg pyridine)		
B	y=0.0016x+0.0067	0.998
T	y=0.005x+0.8572	0.908
E	y=0.0137x+0.7655	0.962
X	y=0.0266x+1.6832	0.966

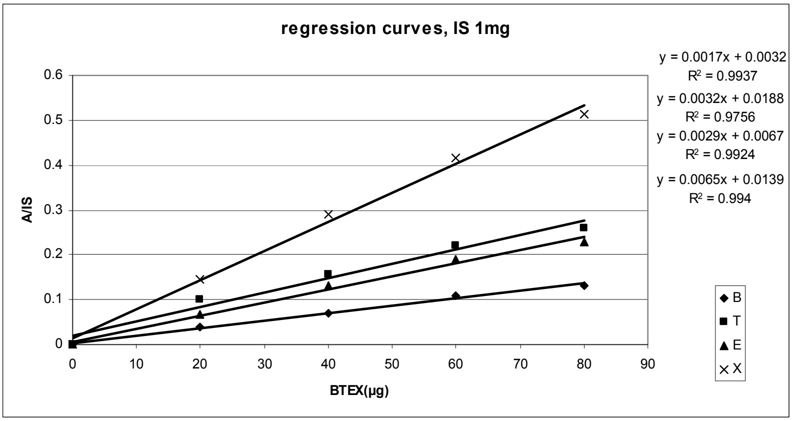

Fig.1. Regression curves for BTEX by using deuterated benzene as the internal standard

Table 2 presents the results obtained for precision and accuracy. A limit of detection of 0.01 μg was obtained for the studied VOCs.

Table 2. Precision and accuracy of the method for indoor air BTEX

Compound	n	Concentration(μg) Added	Measured	Comp/IS	SD	Precision RSD(%)	Accuracy (%)
B	4	40	45.18	0.08	0.01	12.50	12.94
T	4	40	41.00	0.15	0.02	13.33	2.50
E	4	40	42.05	0.13	0.02	15.38	6.29
X	4	40	47.09	0.32	0.06	18.75	17.73
B	3	80	80.47	0.14	0.009	6.43	0.59
T	3	80	91.00	0.31	0.01	3.22	13.75
E	3	80	94.24	0.28	0.02	7.14	17.80
X	3	80	74.28	0.50	0.02	4.0	6.52

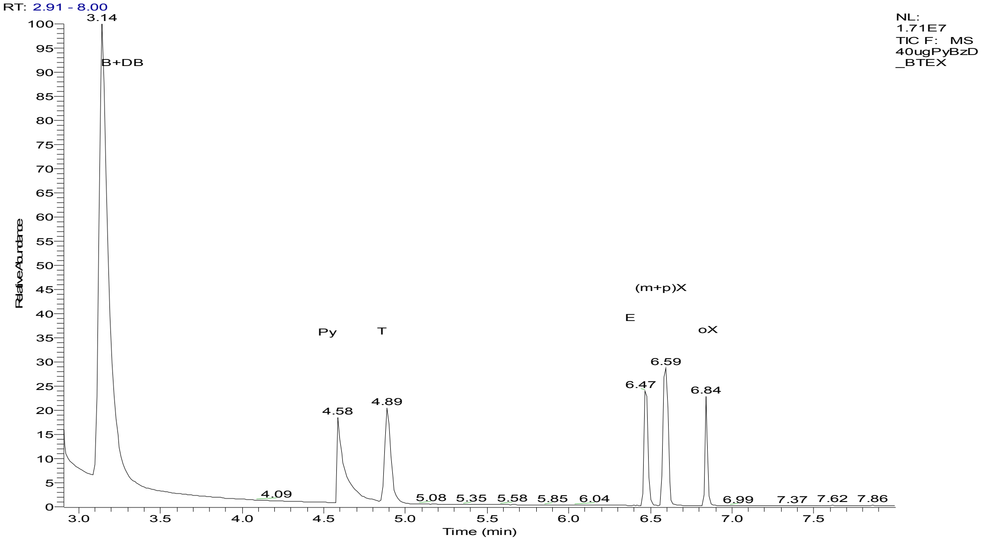

Fig. 2. Chromatographic separation of BTEX and the internal standards, deuterated benzene (DB) and pyridine(Py). The temperature program, 7.5 min: 33°C (2 min), 10°C/min to 70 °C then 50°C/min to 200°C, SIM mode.

The separation chromatogram for BTEX in the SIM mode, with the both internal standards added, is presented in Fig. 2. A 7.5 minutes temperature program was used. Fig. 3 presents the chromatograms of BTEX (SIM mode, the both internal standards added) found in the air samples collected from indoor environment, more precisely: close to an opened new furniture box, in a room with new furniture (1 year old, where a vacuum packed mattress was also placed with the new furniture, one year ago) and a bathroom cabinet (one year old).

Table 3 shows the BTEX levels measured in the air contaminated when new furniture (one year old) is brought into a room of the apartment, as well as the indoor pollutants found in the case of a vacuum packed mattress placed in the same room with the new furniture. The indoor air contaminated in the first days, when the furniture was placed in the room, has been kept into the mattress. By jumping on the mattress, the second column in Table 3, similar BTEX values were obtained as in a new furniture box, first column. Without jumping on the mattress, the indoor air BTEX values extracted are smaller in the room with the furniture bought one year ago, as shown in the third column. In the last column, the levels for indoor air were obtained when the cartridge was placed into a bathroom cabinet, one year old.

Table 3. BTEX (µg m^{-3}) determination in some indoor air measurements (n=2)

Compound	new box	room (mattress)	room	bathroom cabinet
B	2021.8	1314.4	4.9	1017.5
T	938.5	659.7	36.5	546.5
E	14.5	15.7	6.5	7.3
X	54.0	48.7	12.6	35.3

Table 4 compares some indoor air values for BTEX measured inside a parked car (4 years old) under sunlight conditions, with their engines turned on and air conditioner opened (first column) and after ten minutes of ventilation (opened windows). The plastic posters of a laboratory, kept in two poster boxes, gave the BTEX values in the last two columns.

Table 4. BTEX (µg m^{-3}) determination in indoor air extracts, n=2)

Compound	car	vent car	poster box 1	poster box 2
B	13.3	15.9	13.9	15.3
T	101.4	114.0	102.9	135.6
E	22.0	24.4	22.4	33.0
X	31.1	37.4	39.2	51.1

Fig. 3 presents the separation chromatograms of BTEX from indoor air extracts near a new box furniture, the indoor air of an apartment room of 15 m^2 with new furniture (one year old, but jumping on the mattress) and into a bathroom cabinet (one year old).

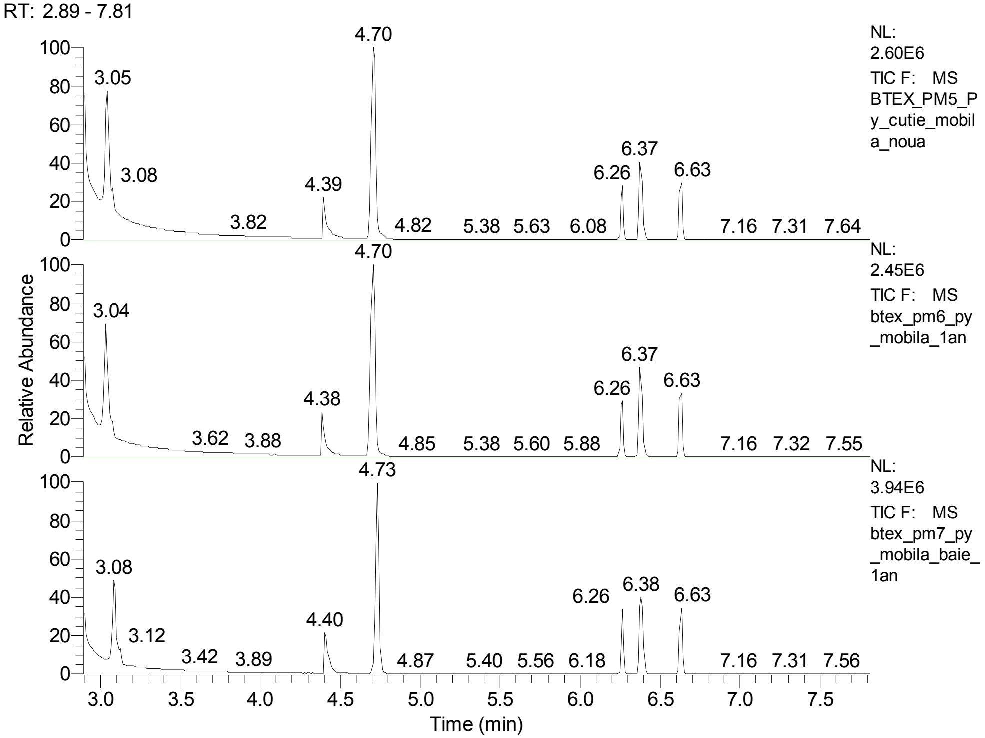

Fig. 3. Separation chromatograms of BTEX from indoor air extracts near a new box furniture, from the indoor air of a small apartment room of 15 m^2 with new furniture (one year old) and into a bathroom cabinet (SIM mode)

The BTEX values presented in Table 3 and 4 are compared in Fig. 4, especially in order to underline the necessity of marking on the vacuum mattress, when inflate, to be fresh air or an empty room, without any contaminants. It is very important to ventilate the rooms with new furniture, especially in the case of small children rooms.

The BTEX levels in the above applications were also calculated by using pyridine as internal standard and similar results have been obtained.

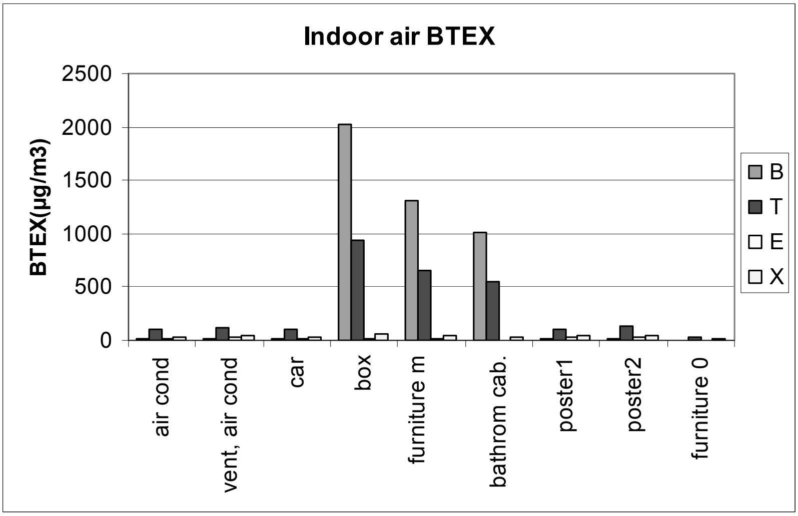

Fig. 4. Comparison of BTEX values (car indoor air, room indoor air, poster boxes; furniture m: jumping on the mattress; furniture 0: no jumping)

The mass spectrometer operating in the SIM mode gave a high selectivity and specificity to the method developed, which allowed the peak deconvolution of benzene and its deuterated analogue internal standard, as they were co-eluting in the total ion chromatogram. Also SIM mode offers higher sensitivity than the scan mode. The validation of the method gave good values for precision, R.S.D. of 3.02 – 18.75 % and accuracy, between 0.59 - 17.8%

The SIM-GC/MS method gave selectivity and specificity allowing the peak deconvolution of benzene and its isotopically labeled analogue. The validation of the method gave good values for precision, R.S.D. lower than 18.75 % and accuracy, lower than 17.8%. The limit of detection for BTEX was of 0.01µg. By using active charcoal cartridges for BTEX determination, the extraction method is rapid and inexpensive.

The method tested for some applications showed BTEX indoor values (µg m^{-3}) in a room and bathroom near new furniture or in the indoor air of a car or boxes containing posters of plastic (Table 3 and 4). Application measurements for precision (R.S.D.) gave lower values than 14 %. The results obtained were higher than BTEX measured in the ambient air in the vicinity of industrial area, where in addition to the traffic emissions, industrial activity enhanced the concentration levels of VOCs [11,15,17,19-21]. The precision of the repeated measurements gave R.S.D. lower than 10 %.

Linearity and precision gave good results in the case of deuterated benzene as internal standard compared with pyridine as internal standard [24]. Similar results for applications were obtained with both internal standards. When the internal standard was deuterated benzene, the intercept values were smaller, consequently we obtained better regression curves.

The BTEX levels inside a parked car, a used vehicle under simulated hot-sunlight conditions, with their engines turned on, showed no apparent health hazard of indoor air of the vehicle. A total of 10.9 mg per cubic meter of VOCs in the new car and 1.2 mg per cubic meter in the old car have been reported [27].

CONCLUSIONS

The GC/MS method developed for BTEX determinations in indoor air is simple, rapid, with high sensitivity, selectivity and specificity. Better linearity was obtained by using deuterated benzene as internal standard than pyridine [24]. The values for BTEX measured close to the new furniture showed higher values than outdoor maximum limit recommended by the European Community, almost the occupational maximum exposure limit. Attention should be paid to room's ventilation and indoor air when inflating a new mattress vacuum packed. Exposure of the sensitive groups as children or pregnant women should be avoided [25-30].

EXPERIMENTAL SECTION

Materials

Carbotrap B, containing active charcoal, was obtained from Supelco, Bellefonte, PA. Deuterated benzene 99.5 atom % was purchased from Alfa Aesar GmBH, Germany. BTEX solution of 2000 ng/ml was purchased from Supelco, Switzerland. All other reagents were from Merck, Germany.

Sample preparation

The cartridges for absorbing BTEX were glass cylinders of 40 mm length, packed with 300 mg of activated charcoal with a particle size of 35–50 mesh. A flow rate of 60 $mL\cdot min^{-1}$ was used for the air samples absorption on active charcoal cartridges. Then the volatiles were extracted in dichloromethane for 2 min. After centrifugation, the internal standard, deuterated benzene (99.5 atom %) was added and 2 µL were injected into the GC.

Method validation

Aliquot samples containing 20, 40, 60 and 80 µg BTEX were adsorbed with a pump on 300 mg active coal at a flow rate of 60 $mL \cdot min^{-1}$ and then were extracted in 1ml dichloromethane. 1mg of deuterated benzene was added as internal standard at each sample. For comparison reason, BTEX standards with pyridine as internal standard was adsorbed in the range 0-100 µg BTEX, in the already published conditions [24].

Apparatus

The determination of the BTEX in air samples was performed by using GC/MS analyses. A Trace DSQ Thermo Finnigan quadrupole mass spectrometer coupled with a Trace GC was used. BTEX and the internal standard were separated on a Rtx-5MS capillary column, 30m x 0.25 mm, 0.25µm film thickness, using a 7.5 min temperature program from $33^{o}C$ (2min), $10^{o}C$/min to $70^{o}C$, then $30^{o}C$/min to $200^{o}C$ in the SIM mode. The following conditions were used: transfer line temperature: $250^{o}C$, injector temperature: $200^{o}C$; ion source temperature $250^{o}C$; Splitter: 10:1. Electron energy was 70eV and emission current, 100µA [24].

The following important ions from the mass spectra of benzene, toluene, ethyl benzene and xylene were used in the SIM mode m/z 78 for benzene, m/z 91 and 92 for toluene, m/z 91 and 106 for ethyl benzene and xylenes [24], and m/z 84 for deuterated benzene. The method was validated in the 0 – 80 µg range and linearity, precision, accuracy and limit of detection parameters were studied.

The regression curves were obtained as a function of the ratio of BTEX standards peaks areas to internal standard (deuterated benzene or pyridine) peak area against the known quantity of the BTEX standards. Quantitation of the BTEX.was performed by adding the same quantitity of the internal standards to the unknown samples and using the calculated regression curves. Benzen was possible to be calculated also by matrix calculation in Excel or isotopic calculation.

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