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SENSITIVE ANALYSIS OF SOME DETRIMENTAL VOLATILE ORGANIC COMPOUNDS IN FABRIC, CARPET AND AIR FRESHENER USING SOLID PHASE EXTRACTION AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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ABSTRACT. Benzene, toluene, ethylbenzene and xylene are known to be lethal environmental contaminants that have carcinogenic and mutagenic influences in human being while styrene and benzaldehyde have a neurotoxic effect. In other hand, the constituents of air freshener considered as a probable source of volatile organic compound. In the present work, a solid phase extraction and gas chromatography–mass spectrometry (GC-MS) technique has been optimized and applied to the fabric, carpet and air freshener samples to determine the trace amounts of benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde. The Supelclean^{TM} ENVI^{TM} - 18 cartridge with dichloromethane extracting solvent were found to be the optimal procedures. The system presented excellent performance in terms of limit of detection (0.08-0.61 ng/mL), coefficient of determination (0.994-0.997), precision with the relative standard deviation values ranging from 0.05-2.57%. According to the results, the concentration of benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde in fresheners' samples was found in the range 0.03-53.27, 0.03-7.12, 0.02-6.51, 0.05-96.44, 0.04-7.06 and 0.22-23.02, respectively. The excellent recovery values were also obtained up to 99.93%. The Supelclean^{TM} ENVI^{TM} - 18 GC-MS system was found to appropriate for the monitoring of analytes in fabric, carpet, air freshener samples, and other samples of the similar constituents.

KEY WORDS: BTEX, Styrene, Benzaldehyde, Air freshener, Solid phase extraction, Gas chromatography–mass spectrometry

INTRODUCTION

BTEX, benzene (B), toluene (T), ethylbenzene (E), and xylene (X) are volatile organic compounds (VOCs), and the main industrial diluents repeatedly encountered as industrial pollutants [1, 2]. These constituents are used in petroleum products, paints, leather, rubber, perfume and printing industries [3–6]. A discharge a high quantity of BTEX polluted wastewater that is released into our surrounding leading to the threat of human exposure [5–7].

At present, numerous marketable products are broadly used in various indoor spaces and to sustain sensory or hygiene environment [8]. Nevertheless, many of such products for instance air fresheners have been exposed to be the main indoor air contaminants sources that release different VOCs, and that may be legally responsible for human health effects [6]. Comprehensible guidelines for such products have not been established by the regulating agencies. However, BTEX exposure is linked with the adverse influences on the liver, central nervous system, heart, and kidneys [9]. The United States Environmental Protection Agency (USEPA) has established maximum BTEX permissible limits in other matrices for instance drinking water, at 0.005, 1, 0.7,

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*Corresponding authors. E-mail: hmali@ju.edu.sa and 10 µg/mL, respectively [10]. The International Agency for Research on Cancer (IARC) has also listed benzene as carcinogenic to humans (Group 1), ethylbenzene as possibly carcinogenic to humans (Group 2B). However, toluene and xylene has not been classified and placed in Group 3 [11]. Among them, the benzene exposure is extensively recognized to proliferation the threat of cancer for instance hematopoietic and leukemia.

Styrene is a substance used in the manufacture of synthetic rubber, polystyrene resins and latex [12, 13]. As a result of automobile and industries exhaust, burning of styrene polymers and cigarette smoke, styrene is released into the air [12, 14]. In humans, styrene is largely oxidized by cytochrome P450, resulting in styrene oxide [15]. Styrene is deliberated to be lethal, mutagenic and possibly carcinogenic to human, and the USEPA has categorized styrene to be an alleged contaminant to the respiratory system, kidney, gastrointestinal tract [15, 16]. In various contexts, regulatory bodies describe styrene as a possible or potential carcinogen for humans. According to the IARC, styrene is "probably carcinogenic to humans" [17].

Benzaldehyde is an unpretentious descriptive of the aromatic aldehydes, arising naturally as a glycoside amygdalin [18]. The synthetic benzaldehyde predominantly used in the production of dyes, unsaturated carboxylic acid mainly cinnamic acid, and to certain level in cosmetics, air freshener, flavoring agents [18, 19]. Only seven cosmetic products currently contain it, with air freshener containing the highest concentration of 0.5% [18, 19]. A variety of off-gassing sources, including wood-based building materials, emits benzaldehyde [18]. These comprise fabric softeners, particleboard, fireboard, floor lacquers and some molded plastics, along with dishwashing liquids, adhesives, fabric softeners, carpet cleaners, glues [18, 19]. In bacterial assays, benzaldehyde produced no mutations, nevertheless produced chromosomal defects in hamster cells and augmented mutations in a mouse lymphoma [18]. In order to ensure the protection of people's health, it is crucial to implement a dependable method for detecting and quantifying trace amounts of BTEX, styrene, and benzaldehyde in air fresheners.

Due to low presence of BTEX, styrene, and benzaldehyde, analysis poses quite a challenge due to sample loss using traditional techniques [5, 20–24]. The development of solid phase extraction (SPE) columns for liquid sample cleanup, extraction, and preconcentration is presently of considerable interest. Thus, a solid phase extraction (SPE) and gas chromatography–mass spectrometry (GC-MS) method was optimized for the analysis of BTEX, styrene and benzaldehyde in fabric, carpet and air fresheners. To our awareness, this is the first study relating to the determination of BTEX, styrene and benzaldehyde in fabric, carpet and air freshener samples.

EXPERIMENTAL

Chemicals and materials

Benzene (≥99.9%), toluene (≥99.9%), ethylbenzene ≥99.5% (GC), xylene (≥98.5%), styrene (≥99%), benzaldehyde (≥99%), benzene-D6 (≥99.0%, internal standard), dichloromethane, acetonitrile, n-hexane and methanol were obtained from Sigma-Aldrich (St. Louis, USA). Solid-phase extraction (SPE) cartridges Supelclean^{TM} ENVI^{TM} - 18 SPE Tube (bed wt. 500 mg, volume 3 mL), Supelclean^{TM} LC-Florisil$^{®}$ SPE Tube (bed wt. 1 g, volume 6 mL), Supelclean^{TM} LC-Si SPE be (bed wt. 500 mg, volume 6 mL) brought from Supelco (Bellefonte, PA, USA).

Fabric, carpet and air freshener samples

Fabric, carpet and air freshener samples were purchased from local markets in Jouf region, Saudi Arabia. Forty-one freshener samples comprising twenty-two fabric and carpet freshener samples and nineteen spray air fresheners (compressed). The description of the studied fabric, carpet and air freshener samples has been demonstrated in Table 1.

Table 1. Description of the studied fabric, carpet and air freshener samples.

Type	Code	Labeled contents	Origin	Brand name
Fabric & carpet freshener	1	Not described	Not described	Rawaa
	2			Arij
	3			Lekaa
	4			Alghalya
	5		Jordan	Nouf-flowers
	6		Jordan	Nouf lavender
	7		Jordan	Nouf - chanel
	8	Water, perfume, benzalkonium chloride, polysorbate 20, methylisothiazolinone, methylchloroisothiazolinone	Jordan	Juhaina- Fresh green
	9	Water, alcohol, perfume, perfume fixative, coloring agent	Jordan	Bader- spring rose
	10			Bader- chanel
	11	Aqua water, ethanol, perfume, polysorbate, methylisothiazolinone, methylchloroisothiazolinone	UAE	SAH- cotton
	12	Demineralized water – fragrance, solubilizer free from alcohol	India	AlKasr - zahrat banafsag
	13			AlKasr - sultan Al Oud
	14			AlKasr - rumbari
	15			AlKasr - banafasal Sabaia
	16			AlKasr - lotus flower blossom
	17			AlKasr - vanilla rich chocolate
	18			AlKasr -majestic
	19			AlKasr - awedony
	20			AlKasr- sweet girl
	21			AlKasr - ful
	22			AlKasr - khurafi
Spray air freshener	23	Butane, isobutene, propane, alcohol denat, perfume, benzyl salicylate, hexylcinnamal, sodium benzoate, sodium nitrite	UAE	La rose defaan -red plum
	24		UAE	La rose de faan- gold silk
	25	Alcohol denat, perfume, butane, isobutene, propane	UAE	Aura - jasmine
	26		UAE	Aura -floral fruit
	27		UAE	Aura classy- green apple
	28		UAE	Aura- lemon citric harmony
	29		UAE	Aura classy cool air
	30		UAE	Aura classy- berry berry
	31		UAE	Aura classy- rose al taifi
	32	Secondary alcohol, fragrance and propellant	KSA	Le cottage - flowers
	33		KSA	Le cottage- jasmine
	34		KSA	Le cottage- kiwi
	35		KSA	Le cottage - muskmelon
	36	Butane, propane, alcohol denat, parfum, dipropylene glycol, alpha-isomethyl ionone,	UAE	Lattafa -24 carat pure gold

	37	benzyl alcohol, benzyl benzoate, benzyl salicylate, citral, citronellol coumarin, eugenol, famesol, geraniol, hydroxyisohexyl 3-cyclohexane carboxaldehyde, evernia prunastri (oakmoss) extract, limonene, linalool	UAE	Lattafa -ser al ameer
	38		UAE	Lattafa- sheikh shuyukh
	39		UAE	Lattafa -ejaazi
	40		UAE	Lattafa - oud mood
	41		UAE	Lattafa- Raghba
UAE, United Arab Emirates; KSA, Kingdom of Saudi Arabia				

Analysis fabric, carpet and air freshener samples

In order to estimate the individual calibration curves and to perform the quantification of the studied compounds, BTEX, styrene and benzaldehyde stock solutions were prepared at level of 200 µg/mL in dichloromethane, used for further dilution purposes, and mixed altogether at desirable concentrations. Calibration solutions were prepared ranging from 0.1-400 ng/mL (benzene), 0.5–600 ng/mL (toluene), 0.5-500 ng/mL (ethyl benzene and xylene), 1-700 ng/mL (styrene) and 0.5-700 ng/mL (benzaldehyde).

In an optimized extraction procedure, 5 mL (in general) of fabric and carpet freshener samples and 5 mL of spray air freshener samples mixed with 5 mL of methanol were directly poured into the SPE cartridge. The SPE was carried out using an assembly of three cartridges: Supelclean$^{\mathrm{TM}}$ ENVI$^{\mathrm{TM}}$ - 18 SPE Tube (bed wt. 500 mg, volume 3 mL), Supelclean$^{\mathrm{TM}}$ LC-Florisil$^{®}$ SPE Tube (bed wt. 1 g, volume 6 mL), and Supelclean$^{\mathrm{TM}}$ LC-Si SPE Tube (bed wt. 500 mg, volume 6 mL). The SPE was performed by fixing a cartridge with a rubber stopper with one hole on the top of the vacuum flask connected to an oil-free vacuum pump by PTFE hose. The SPE cartridges were conditioned with deionized water (5 mL) and methanol (5 mL). The conditioning solvent and sample were applied to the cartridge sorbent at a flow rate of 2 mL/min. The cartridges were vacuum dried, and elution was carried out with 5 mL of dichloromethane, n-hexane, acetonitrile, or methanol. The final extract was transferred to a glass GC vial and directly injected into the GC-MS.

To measure the effectiveness of the proposed SPE-GC/MS method and matrix effect on BTEX, styrene and benzaldehyde peaks symmetry and intensities, and retention time was performed by means of a quantification standard addition approach that comprise 2 non-fortified and three fortified samples. The levels establishing that the quantities of BTEX, styrene and benzaldehyde rise subsequently after spiking in the investigated samples. Samples were examined in triplicates (n = 3) and estimation processes were performed by means of statistical representations based on ANOVA (analysis of variance). Recovery values of the examined BTEX, styrene and benzaldehyde were estimated from the slope attained between the spiked and obtained amounts from analyzed fabric, carpet and air freshener samples.

Instruments

A gas chromatography-mass spectrometry (GC-MS) analysis was conducted using a Trace-1310 GC equipped with a single quadrupole mass spectrometer (ISQLT) and an auto-sampler (AI/AS1310, Thermo Scientific, Waltham, USA). Compounds were separated using a capillary column (DB-624 fused silica) with dimensions of 60 m length, 0.25 mm internal diameter, and 1.4 µm thickness (Agilent Technologies, Santa Clara, CA, USA). The temperature program applied was as follows: initial temperature of 40 °C (held for 1 min), followed by a ramp to 180 °C at a rate of 10 °C/min (held for 2 min), and then a further increase to 240 °C at a rate of 90 °C/min (held for 5 min). The flow rate of helium (carrier gas) was maintained at 100 kPa. The injector, transfer line, and ion source temperatures were set to 250, 230, and 210 °C, respectively. The ion source operated in electron ionization mode at 70 eV. A 1 µL volume of the sample was injected in splitless mode. Compound identification was performed using the mass spectrometer system. Data acquisition, recording, method operation, and data handling were controlled by Xcalibur 3.1 software (Thermo Scientific, Waltham, USA). The National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) mass spectral database was employed for compound identification. Electron ionization mass spectra were scanned in the range of 20 m/z to 150 m/z, and quantification was based on selected ion monitoring (SIM). The representative ions are detailed in Table 2.

Table 2. Retention time, time window and quantification ions for the studied compounds.

Name	RT (min)	Window (min)	Mass (*m/z*)
Benzene	13.40	0.8	78, 51
Benzene-D6	13.60	0.8	84, 56
Toluene	15.75	0.5	92, 91, 65
Ethylbenzene	17.80	0.5	106, 91
Xylene	17.92	0.5	106, 91
Styrene	18.48	0.5	104, 78
Benzaldehyde	20.37	0.8	106, 105, 77

RESULTS AND DISCUSSION

SPE optimization

The development of precise and accurate analytical techniques is essential to advance knowledge about the existence, actions and properties of BTEX, styrene, and benzaldehyde in all areas of interest [5, 21]. Methods that reduce the use of organic solvents, or those that use less, are becoming increasingly popular and may change the way analytical methods are developed [5, 21]. In addition to the speed and simplicity of SPE technique, it eliminates the disadvantages associated with conventional extraction methods, such as long operation times and large solvent volumes [21, 25, 26]. Therefore, the use of SPE has been proposed as alternatives to traditional methods for the preparation of samples in the current work. As far as our knowledge extends, this represents the inaugural report concerning the identification of BTEX, styrene and benzaldehyde in fabric, carpet and air freshener samples using SPE-GC/MS technique. Initially, we have used three types of SPE cartridges including Supelclean™ ENVI™ - 18 SPE with matrix silica gel base material (acid washed, irregular shaped), Supelclean™ LC-Florisil® SPE with matrix magnesium silicate base material and Supelclean™ LC-Si SPE with silica gel base material (irregularly shaped). To achieve the maximum compounds recovery rates with least possible impurity, primarily the extraction method was carried out on a mixture of aqueous standard solution of BTEX, styrene and benzaldehyde (1 µg/mL) using three SPE cartridges individually. At first, the extraction cartridges were preconditioned by means of water (5 mL) and methanol (5 mL) respectively, followed by drying under vacuum. Then, 5 mL standard mixture solution were passed through each cartridge at controlled flow rate. Afterwards, acetonitrile, methanol, n-hexane, and dichloromethane were used as extracting solvents separately for each cartridge to elute the adsorbed compounds. According to various trials, the adsorbed compounds was completely eluted with good recovery percentage by using dichloromethane. To choose the suitable adsorbent material, three types of cartridges included Supelclean™ ENVI™ - 18 SPE, Supelclean™ LC-Florisil® SPE and Supelclean™ LC-Si SPE was selected for suitable extraction of all compounds and the results were displayed in Figures 1 and 2.

According to the results, the average recovery percentages of benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde were 80.14, 83.75, 101.21, 32.93, 74.33 and 59.49%, respectively, in case of supelclean LC-Florisil SPE. While in case of supelclean LC-Si SPE, the average recovery percentages found to be 90.61, 18.54, 34.41, 13.41, 93.81 and 74.97% for benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde, respectively. The last cartridge (Supelclean^{TM} ENVI^{TM} - 18 SPE) in total, exhibited a good recovery for all analytes as shown in Table 3.

So, the Supelclean^{TM} ENVI^{TM} -18 SPE with dichloromethane was chosen to be the best cartridge and extracting solvent, respectively due to its good recovery and low interferences with dichloromethane. The system provided best recovery rates up to 99.93% comprising of other quality parameters LOD (0.08-0.61 ng/mL), R^2 (0.994-0.997), precision (RSD, 0.05-2.57%.).

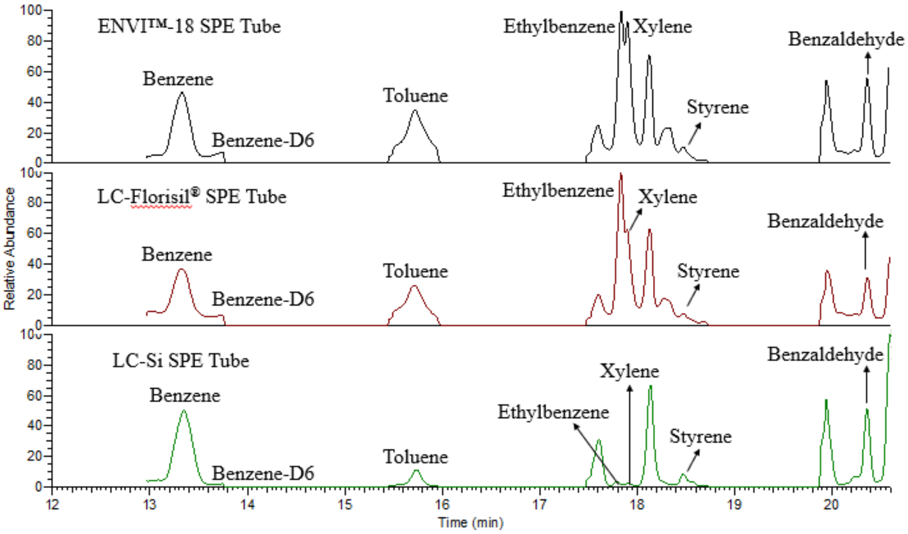

Figure 1. GC-MS chromatograms of benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde at different types of cartridges.

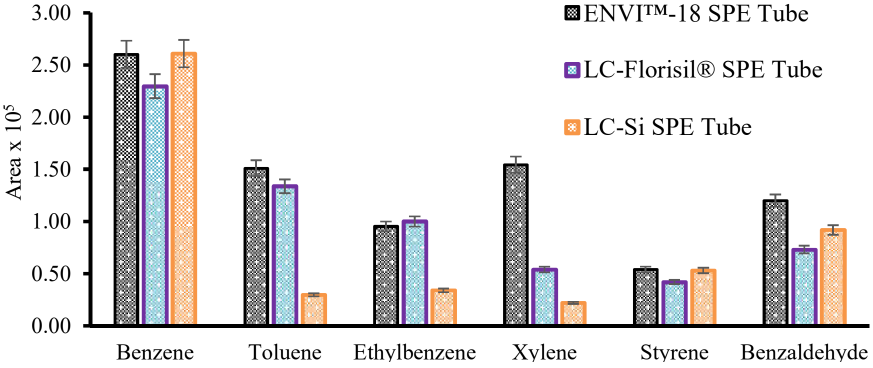

Figure 2. Peak area of each analyte at different types of cartridges.

In addition, Supelclean^{TM} ENVI^{TM} - 18 SPE-GC-MS method has reduced the sample manipulation and extraction by nearly four-fold likened to the traditional SPE method [27–29]. Thus, the optimized method (Supelclean^{TM} ENVI^{TM} - 18 SPE-GC-MS) was effectively utilized to the examination of BTEX, styrene and benzaldehyde in numerous real samples comprising fabric, carpet and air fresheners. The samples were categorized in two groups such as aerosol (samples 1-22) and pressurized types (samples 23-41). The description of the samples has been demonstrated in Table 1. As aerosols contain water, 5 mL of each type of aerosol sample was mixed with IS (50 ng/mL) and passed through a Supelclean^{TM} ENVI^{TM} - 18 cartridge with a flow rate of 2 mL/min to extract the samples. Following extraction, 5 mL of dichloromethane was used to elute the organic compounds. For pressurized type, since there is no water present, 5 mL of each sample was mixed with 5 mL of methanol for stabilization, then IS (50 ng/mL) was added, passing through a Supelclean^{TM} ENVI^{TM} - 18 cartridge with a flow rate of 2 mL/min, collected in falcon tubes, filtered and introduced into the GC. The volume of sample (1 μL) was introduced into the GC-MS system.

Table 3. Results of assay validation parameters of the proposed GC-MS method for the determination of BTEX, styrene and benzaldehyde.

Parameter	Benzene (ng/mL)	Toluene (ng/mL)	Ethyl benzene (ng/mL)	Xylene (ng/mL)	Styrene (ng/mL)	Benzaldehyde (ng/mL)
Range	0.1-400	0.5-600	0.5-500	0.5-500	1-700	0.5-700
Slope	$1.4x10^4$	$2.83x10^4$	$2.12x10^4$	$9.64x10^3$	$1.4x10^4$	$1.6x10^4$
Intercept	$2x10^5$	$4.34x10^5$	$2.84x10^5$	$1.37x10^5$	$-1.48x10^5$	$-6.9x10^4$
R^2	0.998	0.996	0.997	0.997	0.994	0.995
LOD	0.08	0.09	0.47	0.34	0.61	0.09
LOQ	0.25	0.31	1.57	1.13	2.03	0.30
Recovery%	90.23-98.90	94.27-99.62	96.87-98.80	94.08-99.69	95.66-97.67	97.36-99.93
RSD%	0.41-1.37	0.25-1.76	0.25-1.66	0.68-1.01	0.05-1.49	0.27-2.57

LOD = limit of detection (SD of the response/slope) × 3; LOQ = limit of quantification (SD of the response/slope) × 10; RSD, relative standard deviation.

Analytical figures of merit

To evaluate the performance of the optimized technique various quality parameters for instance limit of detection (LOD), limit of quantification (LOQ), linearity, and precision have been studied. LOD and LOQ were evaluated by signal-to-noise ratio of 3 and 10, respectively [30]. Precision was assessed in terms of repeatability (run-to-run, five replicate analyses of the same standard mixture solution within one day) and reproducibility (day-to-day, five replicate analyses over three consecutive days) of the same standard mixture solution. Results of assay validation parameters of the suggested GC-MS technique for the analysis of BTEX, styrene and benzaldehyde have been demonstrated in Table 3. According to the results in Table 3, the linearity of benzene, toluene, ethyl benzene, xylene, styrene and benzaldehyde was confirmed in the range of 0.1-400, 0.5-600, 0.5-500, 0.5-500, 1-700 and 0.5-700 ng/mL, respectively. The limit of detection (LOD) was 0.08, 0.09, 0.47, 0.34, 0.61 and 0.09 ng/mL of benzene, toluene, ethyl benzene, xylene, styrene and benzaldehyde, respectively, ensuring the sensitivity of developed method. In addition, the values of percentage recovery and RSD of analytes varied from 90.23 to 99.93% and 0.05 to 2.57%, respectively, indicating the accuracy and precision of the developed method

Application to freshener samples

Forty-one freshener samples comprising twenty-two fabric and carpet fresheners and nineteen spray air fresheners (compressed) of different brands were studied. The outcomes have been presented in Table 4. The approach was used for the estimation of real samples including fabric, carpet and air freshener samples, BTEX found not detected (nd) to 96.44 ng/mL, whereas styrene and benzaldehyde were found nd-7.06 ng/mL and nd-23.02 ng/mL, respectively.

Among the determined BTEX, styrene and benzaldehyde levels in fabric, carpet and air freshener samples, the benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde were found at higher levels in some samples for instance sample 22 (53.27 ng/mL), sample 8 (7.12 ng/mL), sample 1 (6.51 ng/mL), sample 11 (96.44 ng/mL), sample 5 (7.06 ng/mL) and sample 6 (23.02 ng/mL), respectively. As an example, the GC-MS chromatogram of the studied sample has been demonstrated in Figure 3. In agreement to the earlier available work [31], Lim *et al.* have studied the BTEX in 207 consumer products using headspace-GC/MS, found in 59 samples at higher concentration levels [31] which is differing to the outcomes achieved in the present study. However, based on the current literature survey, most of the studies have reported the presence of BTEX, styrene, and benzaldehyde in various matrices utilizing the SPE-GC/MS technique. The studies include indoor and outdoor air [32–34], waste water and human hair [35], hookah smoke [36], water and milk [21], French soils irrigated with agro-industrial wastewater [37], ABS plastic toys [38], yoghurt [39], and plastic food containers [40].

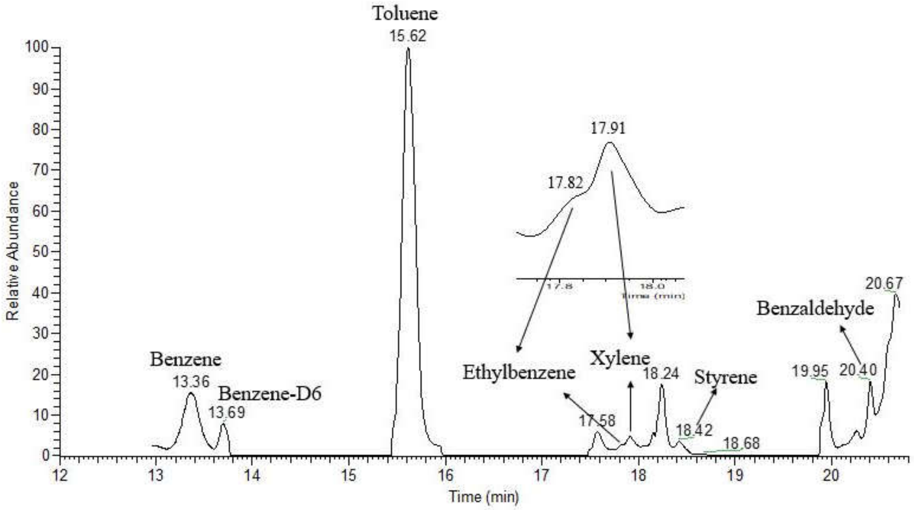

Figure 3. GC-MS chromatogram of benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde in fabric and carpet freshener sample no. 10.

Table 4. Levels of BTEX, styrene and benzaldehyde in fabric, carpet and air freshener samples.

Sample code	Benzene (ng/mL ± sd)	Toluene (ng/mL ± sd)	Ethylbenzene (ng/mL ± sd)	Xylene (ng/mL ±sd)	Styrene (ng/mL ± sd)	Benzaldehyde (ng/mL ± sd)
1	1.73 ± 0.090	1.60 ± 0.048	6.51± 0.051	nd	0.44 ± 0.002	7.74 ± 0.017
2	0.63 ± 0.028	1.15 ± 0.047	0.05 ± 0.001	8.52 ± 0.070	0.05 ± 0.001	1.40 ± 0.002
3	1.65 ± 0.110	0.90 ± 0.031	0.16 ± 0.002	1.11 ± 0.023	0.66 ± 0.001	6.82 ± 0.041
4	nd	5.68 ± 0.510	nd	16.27 ± 0.053	nd	7.02 ± 0.023
5	nd	0.28 ± 0.010	0.07 ± 0.001	0.33 ± 0.002	7.06 ± 0.052	11.4 ± 0.036
6	1.08 ± 0.011	0.16 ± 0.030	nd	0.09 ± 0.001	0.81 ± 0.004	23.02 ± 0.025
7	1.88 ± 0.090	3.80 ± 0.048	nd	6.48 ± 0.017	0.67 ± 0.005	5.38 ± 0.054
8	nd	7.12 ± 0.210	nd	nd	0.10 ± 0.003	nd
9	nd	0.70 ± 0.015	nd	nd	1.07 ± 0.009	2.65 ± 0.026

10	0.35 ± 0.007	0.08 ± 0.003	0.23 ± 0.002	0.12 ± 0.003	0.26 ± 0.001	6.67 ± 0.055
11	2.08 ± 0.015	3.76 ± 0.280	nd	96.44 ± 0.083	1.19 ± 0.005	7.33 ± 0.032
12	nd	0.34 ± 0.006	nd	2.98 ± 0.011	nd	1.90 ± 0.038
13	nd	1.05 ± 0.012	nd	6.59 ± 0.048	nd	nd
14	2.52 ± 0.021	0.24 ± 0.004	0.14 ± 0.001	0.67 ± 0.008	0.72 ± 0.004	2.34 ± 0.013
15	nd	0.09 ± 0.001	4.50 ± 0.071	7.15 ± 0.045	2.79 ± 0.081	5.64 ± 0.031
16	1.22 ± 0.050	0.19 ± 0.014	0.52 ± 0.002	0.81 ± 0.001	0.84 ± 0.007	nd
17	1.81 ± 0.022	0.63 ± 0.014	1.35 ± 0.012	1.52 ± 0.01	0.15 ± 0.002	3.08 ± 0.055
18	0.35 ± 0.005	0.13 ± 0.003	0.02 ± 0.001	0.05 ± 0.001	0.39 ± 0.002	nd
19	0.55 ± 0.002	0.13 ± 0.006	nd	nd	0.62 ± 0.002	2.07 ± 0.019
20	0.91 ± 0.007	1.99 ± 0.058	nd	nd	nd	8.73 ± 0.019
21	3.05 ± 0.025	1.77 ± 0.070	3.59 ± 0.082	3.02 ± 0.008	nd	14.24 ± 0.055
22	53.27 ± 0.052	0.69 ± 0.01	nd	nd	2.65 ± 0.024	4.46 ± 0.034
23	1.43 ± 0.013	0.13 ± 0.001	nd	7.33 ± 0.027	5.07 ± 0.085	1.72 ± 0.017
24	nd	0.07 ± 0.003	nd	0.39 ± 0.002	nd	0.33 ± 0.001
25	1.25 ± 0.016	0.12 ± 0.004	nd	nd	nd	1.92 ± 0.008
26	nd	0.11 ± 0.007	nd	nd	nd	nd
27	0.16 ± 0.001	0.46 ± 0.013	0.59 ± 0.002	1.35 ± 0.004	0.92 ± 0.003	nd
28	0.17 ± 0.003	nd	nd	nd	nd	nd
29	0.15 ± 0.001	0.16 ± 0.004	0.03 ± 0.001	0.13 ± 0.005	0.11 ± 0.001	nd
30	nd	0.39 ± 0.041	0.28 ± 0.003	0.93 ± 0.003	nd	nd
31	0.32 ± 0.002	0.74 ± 0.009	0.27 ± 0.003	0.70 ± 0.001	nd	nd
32	0.65 ± 0.002	0.45 ± 0.004	nd	nd	nd	nd
33	0.75 ± 0.002	0.59 ± 0.018	0.06 ± 0.001	1.31 ± 0.009	0.92 ± 0.003	1.34 ± 0.012
34	nd	2.11 ± 0.068	nd	1.54 ± 0.018	nd	nd
35	0.57 ± 0.001	0.80 ± 0.015	nd	0.90 ± 0.002	0.05 ± 0.001	16.15 ± 0.013
36	21.21 ± 0.029	0.12 ± 0.005	nd	5.82 ± 0.013	2.54 ± 0.017	5.44 ± 0.045
37	0.09 ± 0.001	0.04 ± 0.002	0.09 ± 0.001	0.68 ± 0.006	0.07 ± 0.001	nd
38	0.04 ± 0.001	0.06 ± 0.001	0.03 ±0.001	0.13 ± 0.001	0.04 ± 0.001	0.84 ± 0.003
39	0.03 ± 0.001	0.07 ± 0.001	0.05 ± 0.001	0.22 ± 0.001	0.09 ± 0.001	0.22 ± 0.002
40	nd	0.04 ± 0.005	0.26 ± 0.001	1.09 ± 0.021	0.74 ± 0.006	0.22 ± 0.001
41	nd	0.03 ± 0.006	0.07 ± 0.002	0.50 ± 0.006	1.25 ± 0.067	0.33 ± 0.001

sd, standard deviation (n = 3).

Comparison with other methods

The linear range and LOD values for the proposed method for the determination of benzene, toluene, ethylbenzene, xylene, styrene and benzaldehyde were compared with those of previously reported approaches, as shown in Table 5. In general, the developed Supelclean^{TM} ENVI^{TM} - 18 - GC-MS method has the merits of considerable linear range and good sensitivity. Also, it has a good separation efficiency, considerable analysis speed and elevated preconcentration of six analytes where are not presented in the reported methods.

Table 5. Comparison of the proposed method with some reported methods.

Instrument	Component	Linear range (ng/mL)	LOD (ng/mL)	Applications	Ref
Gas chromatography/flame ionization detection	Benzene	0.05–500	0.015	Milk and water	21
	Toluene				
	Ethylbenzene				
	Xylene				
Gas chromatography / flame ionization detection	Benzene	5–200	1.6	--	41
	Toluene	5–200	1.6		

	Ethylbenzene	2–200	0.6		
	Xylene	2–200	0.6		
Gas chromatography / flame ionization detection	Benzene	0.1–100	0.027	Water	42
	Toluene		0.054		
	Ethylbenzene		0.012		
	Xylene		0.031		
Headspace-gas chromatography/mass spectrometry	Benzene	2,500–25,000	7.5	Bovine teeth	20
	Toluene		1.1		
	Ethylbenzene		0.2		
	Xylene		0.2		
Gas chromatography/ mass spectrometry	Benzene	0.1 to 2.0	0.019	Freshly fallen snow	27
	Toluene		0.024		
	Ethylbenzene		0.018		
	Xylene		0.021		
Cryo-trap- gas chromatography/mass spectrometry	Benzene	0.0001–50	0.00004	Water	29
	Toluene		0.00002		
	Ethylbenzene		0.00005		
	Xylene		0.00001		
Gas chromatography/mass spectrometry	Benzene	-	0.3	Soil	37
	Toluene		0.5		
	Ethylbenzene		1.6		
	Xylene		0.9		
Gas chromatography/mass spectrometry	Benzene	0.1-400	0.08	Fabric, carpet and air freshener	CM
	Toluene	0.5-600	0.09		
	Ethylbenzene	0.5-500	0.47		
	Xylene	0.5-500	0.34		
Gas chromatography/ flame ionization detection	Benzadehyde	1.0-1000	0.2	Preservative (benzyl alcohol)	43
Capillary gas chromatography		500-100,000	130		44
Micellar liquid chromatography		1,000–20,000	120		45
Gas chromatography/ mass spectrometry		1-700	0.61	Fabric, carpet and air freshener	CM
Headspace-gas chromatography/mass spectrometry	styrene	-	7	Food simulants	46
Gas chromatography-mass spectrometry		5.06–440	1.54	Honey	47
Gas chromatography-mass spectrometry		0.5-700	0.09	Fabric, carpet and air freshener	CM
CM: current method					

CONCLUSION

A novel approach utilizing SPE and GC-MS has been fine-tuned and implemented for the detection of BTEX, styrene and benzaldehyde in fabric, carpet and air freshener samples. Extraction method was tested out on three different base material SPE cartridges (Supelclean^{TM} ENVI^{TM} -18 SPE Tube, Supelclean^{TM} LC-Florisil® SPE Tube and Supelclean^{TM} LC-Si SPE Tube) and extracting solvents (dichloromethane, n-hexane, acetonitrile, or methanol). Among them, the Supelclean^{TM} ENVI^{TM} - 18 SPE with dichloromethane extracting solvent were found to be the optimal SPE method in combination with GC-MS. The system has offered excellent performance comprising LOD (0.075-0.61 ng/mL), R^2 (0.994-0.997) and precision (0.05-2.57%) values. The adequate recovery values were also obtained up to 99.93%. The Supelclean^{TM} ENVI^{TM} - 18 - GC-MS system was found to appropriate for the monitoring of BTEX, styrene and benzaldehyde particularly in fabric, carpet and air freshener samples (41 samples) collected from Saudi Arabia markets. Finally, no sample was found to be completely free of all analyte. In other hand, benzene, styrene and benzaldehyde were detected in 28 samples, toluene in 40 samples, ethyl benzene in 21 samples and xylene in 32 samples.

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