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Production of *in situ* mixed gas phase volatile organic compound standards for sorbent tube applications

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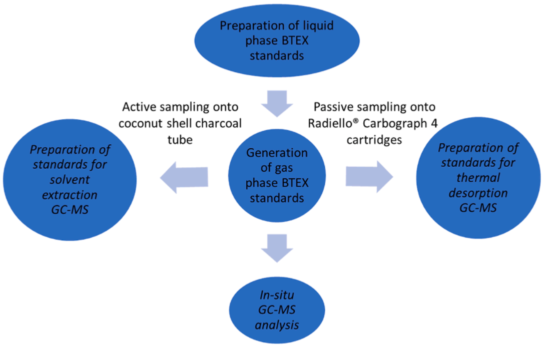
GRAPHICAL ABSTRACT



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ABSTRACT

Volatile organic compounds (VOCs) are a significant class of air pollutants, as they pose a risk to human health and the environment. Precise quantification of VOCs sampled onto sorbent tubes requires gas phase standards at suitable concentrations. Herein, we present a:

- gas standard preparation method for benzene, toluene, ethylbenzene and xylene (BTEX) prepared from liquid standards by means of evaporation and dynamic dilution with nitrogen
- demonstration of the applicability of the LiqMix Cascade gas mix system.

Repeatability and reproducibility were first successfully demonstrated via direct GC–MS analysis of generated gas mixtures. Then μg levels of generated gas standards were adsorbed onto sorbent tubes employed in active sampling and ng levels were collected onto Radiello cartridges used in passive sampling, followed by liquid extraction or thermal desorption and GC–MS analysis. Accuracy was verified by a BTEX certified reference material (99 % recovery). The LiqMix

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Cascade gas mix system was shown to produce precise and repeatable concentrations of BTEX gas phase standards for sorbent tube sampling applications for the first time.

Specifications table

Subject area	Chemistry
More specific subject area	Environmental analysis
Name of your method	Sorbent standards preparation for VOC analyses
Name and reference of original method	None
Resource availability	https://www.alytechme.com/liqmix.html

Background

Volatile organic compound (VOC) gas phase standards are required for the effective evaluation of sorbents and for the generation of truly matrix matched calibration standards, in which the analytes of interest have been introduced onto the sorbents in the gas phase in the same manner as the samples. Regardless of the analytical instrument configurations chosen for analyses, selection of the phase of the standards is an important factor for accurate quantification of VOCs [1]. In practice, liquid phase standards are used more frequently because of several advantages, including low cost, ease of handling and due to the fact that they can be used for a wide range of VOCs. In addition, liquid standards facilitate the employment of the internal standard method, where sorbents are spiked with a VOC standard [1,2]. However, studies have found that when gaseous samples are calibrated against liquid phase standards, biases varied significantly [3,4]. These biases were attributed to matrix effects inherent to liquid standards, where polar VOCs might co-elute with methanol resulting in either an overestimation or an underestimation in calibration accuracy [4,5]. The use of gas phase standards is thus often preferred for the analysis of VOCs in ambient or polluted air [1]. This is because gas phase standards facilitate the elimination or suppression of matrix effects as well as sample loss, which normally act as key experimental variables [1]. Gas phase VOC standards are available in cylinders, however they are expensive and they need to be used in combination with gas flow regulators and mass flow controllers for sorbent adsorption applications [6].

To address these challenges a commercial gas mix instrument called the LiqMix Cascade has recently been designed to produce gas phase standards from liquid phase standards. This system may thus offer an effective way for on-site generation of gas phase standards, including those that are not commercially available in cylinders, such as unstable or reactive compounds, as well as complex multi-component gas mixtures.

We have thus developed a method using the LiqMix to prepare customised gas phase calibration standards of benzene, toluene, ethylbenzene, and xylene (BTEX) for occupational and ambient air monitoring applications, whereby these target analytes were adsorbed onto commercially available sorbent tubes for the first time. Both coconut shell charcoal sorbent with subsequent liquid extraction and Carbograph 4 sorbent with thermal desorption were tested. This approach reduces the cost of analysing ambient air for VOCs by providing on-demand gas phase standard mixtures at varying concentrations, eliminating the high cost of buying gas standard mixtures in cylinders. This in turn reduces the risk associated with high-pressure gas cylinders and provides a safer alternative method for preparation of hazardous gas mixtures. On-demand gas standard preparation also reduces the need for storage and disposal of unused gas mixtures, thereby contributing positively to safety and environmental aspects.

Method details

Chemicals

The BTEX reference gas mixtures were produced from high purity starting materials: 99.9 % benzene (Sigma Aldrich, United Kingdom), 99.9 % toluene (Promark Chemicals, South Africa), 99.9 % ethylbenzene (Sigma Aldrich, United Kingdom) and 99.9 % o-xylene (Sigma Aldrich, United Kingdom). Solvents used were >99 % methanol (Merck Supelco®, Germany) and 99.9 % carbon disulfide (Honeywell™, United Kingdom).

A BTEX liquid standard stock solution was prepared by adding specific masses of the individual components to a 500 mL volumetric

Table 1
Concentrations of BTEX components in the stock standard solution used for gas standard generation.

Analyte	Mass (g)	Moles	Mole (%)	Concentration (mg/L)
Benzene	1.9495	0.0250	0.2042	3899
Toluene	1.9133	0.0208	0.1699	3827
Ethylbenzene	1.9178	0.0181	0.1478	3836
o-Xylene	1.8945	0.0178	0.1460	3789
Methanol	389.65	12.1614	99.3327	779,305

Table 2

LiqMix parameters for the LiqMix *in situ* GC–MS injection for benzene and toluene standards. LiqMix evaporation chamber set at 35 °C.

Parameter	BTEX Gas Standard 1 ($n = 10$)	BTEX Gas Standard 2 ($n = 10$)	BTEX Gas Standard 3 ($n = 5$)	BTEX Gas Standard 4 ($n = 5$)	BTEX Gas Standard 5 ($n = 5$)
Channel 1 BTEX Standard (g/h)	0.664	0.486	1.063	1.022	1.022
Channel 2 Air/N_2 (NmL/min)	1532.8	556.2	1219.2	1168.1	1168.1
Output 1st stage Air/N_2 (NmL/min)	49.8	49.6	47.6	40.2	50.3
Dilution 2nd stage Air/N_2 (NmL/min)	950.2	950.4	590.5	365.7	355.6
Total Flow (NmL/min)	1000.0	1000.0	638.1	405.9	405.9
Benzene (nL/L)	500	1000	1500	2000	2500
Toluene (nL/L)	420	839	1259	1679	2099

Note: nL/L refers to 1 nL of analyte gas diluted in 1 L of nitrogen gas and is equivalent to ppbv.

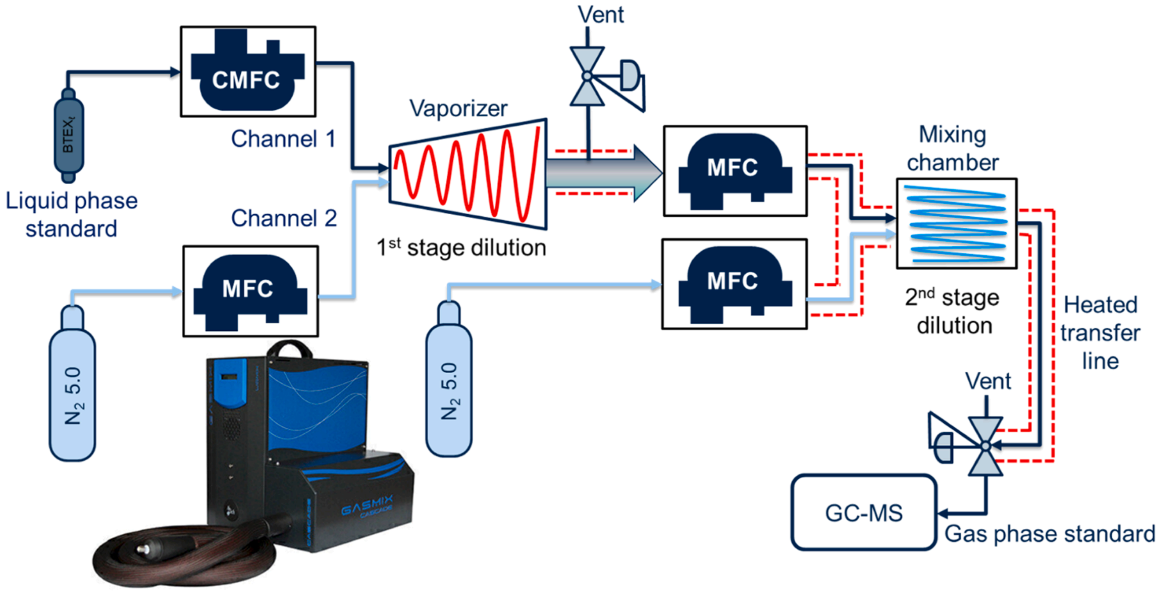

Fig. 1. Schematic of the experimental setup for *in-situ* GC–MS analysis of the gas phase BTEX standards prepared by the LiqMix.

flask and diluting with methanol (Table 1). The standard solution was then transferred into a 500 mL amber Schott bottle for storage. The BTEX standard stock solution was transferred with a 100 mL gas tight syringe into a 75 mL stainless steel cylinder which was connected to the LiqMix Cascade instrument (AllyTech, France) (referred to as Channel 1 BTEX Standard in Table 2) for gas phase BTEX standard preparation.

Basic principles of the LiqMix cascade

The LiqMix Cascade gas mix (Fig. 1) is a system designed for automatic generation of customized calibration gas mixtures by controlled evaporation of liquid standards with dynamic dilution and mixing with one or several gases in two stages [3]. In the first dilution stage, a Coriolis mass flow controller accurately delivers liquid into a vaporizer regulated at the user-defined temperature. The liquid is evaporated into a flow of a carrier gas, which transfers it into a mixing chamber where it can be mixed with other gases introduced by up to four optional mass flow controllers. With a dilution ratio of up to 10^4 at the 1st stage, a pure liquid can be diluted down to 100 ppm. When the Cascade option is enabled, a portion of the gas stream is sent to the second dilution stage and the rest is vented. In the Cascade, the gas is further diluted up to 10 000 times, reducing the analyte concentration down to the ppb level. All interconnections and the outlet line are heated to avoid re-condensation up to the delivery point [3].

In situ testing

Experiments were first conducted at higher BTEX concentrations to test the repeatability and reproducibility of the LiqMix system. This was achieved by directly connecting it to a gas chromatograph - mass spectrometer (GC–MS) for *in-situ* analysis of the BTEX

Table 3
LiqMix parameters for the LiqMix *in situ* GC–MS injection for ethylbenzene and o-xylene standards. LiqMix evaporation chamber set at 60 °C.

Parameter	BTEX Gas Standard 1 ($n = 10$)	BTEX Gas Standard 2 ($n = 10$)	BTEX Gas Standard 3 ($n = 5$)	BTEX Gas Standard 4 ($n = 5$)	BTEX Gas Standard 5 ($n = 5$)
Channel 1 BTEX Standard (g/h)	1.020	1.020	1.017	1.017	1.017
Channel 2 Air/N_2 (NmL/min)	1168.2	1168.2	1168.2	1168.2	1168.2
Output 1st stage Air/N_2 (NmL/min)	34.4	50.3	49.7	50.3	50.3
Dilution 2nd stage Air/N_2 (NmL/min)	965.6	680.9	430.3	314.1	241.3
Total Flow (NmL/min)	1000.0	731.2	480.0	364.4	291.6
Ethylbenzene (nL/L)	500	1000	1500	2000	2500
o-Xylene (nL/L)	494	987	1481	1974	2468

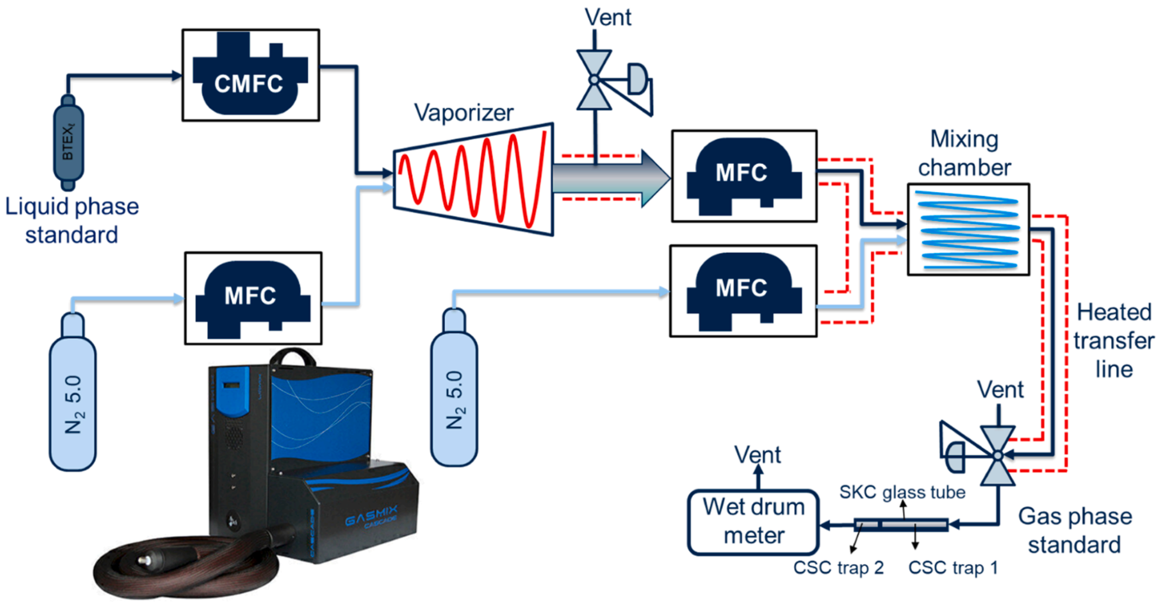

Fig. 2. Schematic of the experimental setup for BTEX gas phase standards preparation with adsorption onto CSC sorbent tubes for solvent extraction with GC–MS analysis.

standards produced by the LiqMix system. The flow from the heated transfer line was split by means of a T-splitter. A needle valve was connected to the side of the split that was connected to the GC–MS to reduce the high flow from the LiqMix (the higher the diluted gas stream, the higher the total flow from the instrument) and the other side of the T-splitter was connected to the vent line as shown in Fig. 1. These *in situ* experiments revealed the need to prepare the standards in batches of benzene and toluene at 35 °C and ethylbenzene and xylene at 60 °C respectively, due to the vapour pressure differences between the BTEX components. The instrument parameters for the gas phase BTEX standard production are shown in Table 2 and Table 3.

Analyses were carried out with an Agilent GC–MS (7890 GC with a 5975C MSD, Chemetrix, South Africa), using a Stabilwax®MS column (60 m × 0.25 mm i.d. × 0.5 µm df). A 1 µL gas injection volume was used by employing a sample loop of this volume which was directly connected to the LiqMix outlet. The oven program began at 40 °C, followed by three temperature ramps: 10 °C/min to 80 °C, then 5 °C/min to 130 °C, and finally 50 °C/min to 320 °C. The inlet temperature was maintained at 280 °C, with a helium carrier gas flow rate of 1.2 mL/min and a split flow of 100 mL/min. The scan range was 35 – 300 amu and ionization was conducted at 70 eV.

Sorbent based standard generation and testing

Carbon-based sorbent tubes for liquid extraction

The *in-situ* analyses were followed by preparation of gas phase BTEX standards adsorbed onto carbon-based sorbents typically used for BTEX active sampling, followed by solvent extraction thereof prior to GC–MS analyses. This was achieved by removing the GC–MS connection to the needle valve and replacing it with sorbent tubes (Fig. 2). A drum type wet gas meter (Ritter®, Germany), was connected to the other end of the sorbent tubes to measure the volume of gas that flowed through the tubes. This allowed for predetermined masses of BTEXs to be adsorbed onto the tubes, as a preset volume of gas was passed through the tube. The gas flow was

Table 4
LiqMix parameters for generation of BTEX gas standards on sorbent tubes for solvent extraction.

Parameter	Value
Channel 1 BTEX Standard (g/h)	0.486
Channel 2 Air/N_2 (NmL/min)	556.2
Output 1st stage Air/N_2 (NmL/min)	49.6
Dilution 2nd stage Air/N_2 (NmL/min)	950.4
Total Flow (NmL/min)	1000
Batch 1 vaporization at 35 °C	
Benzene (µL/L)	1000
Toluene (µL/L)	839
Batch 2 vaporization at 60 °C	
Ethylbenzene (µL/L)	730
o-Xylene (µL/L)	721

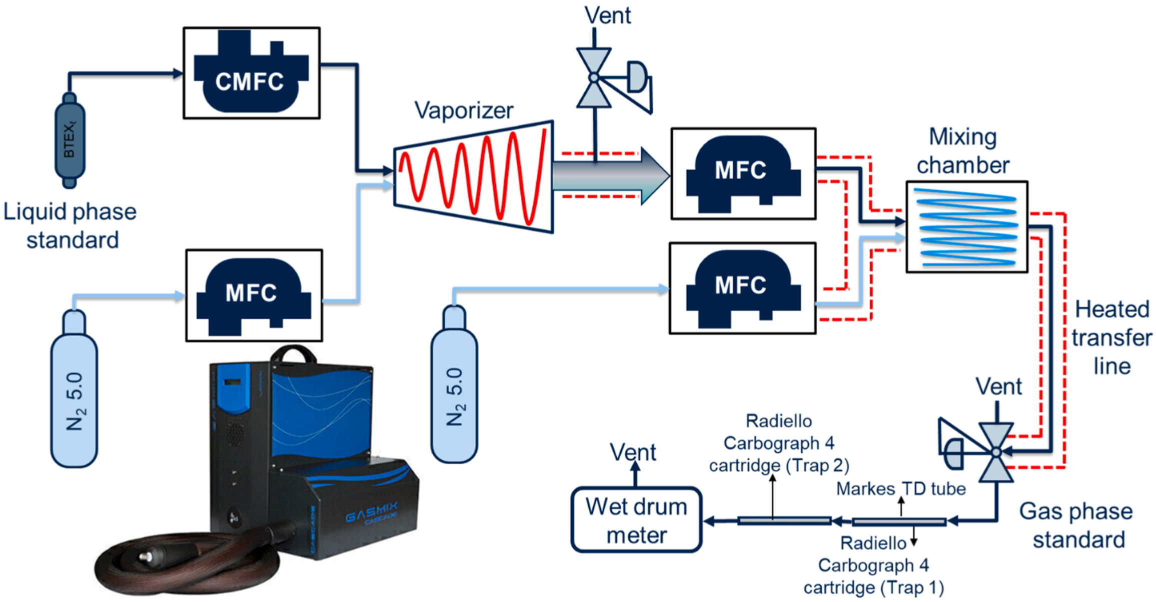

Fig. 3. Schematic of the experimental setup for BTEX gas phase standard preparation with adsorption onto Carbograph 4 cartridges for thermal desorption with GC–MS analysis.

maintained at 200 mL/min by means of a needle valve so as to mimic typical VOC active sampling conditions. Glass tubes packed with Anasorb® coconut shell charcoal (CSC) (SKC, USA) were used for the solvent extraction method (6 mm diameter x 70 mm length, containing two sections of 50/100 mg, 20/40 mesh adsorbing material). These tubes contain a secondary CSC trap to determine any breakthrough of the target analytes from the primary trap during sampling (Fig. 2). For this reason a secondary sorbent tube was not connected to the sampling train. Table 4 shows the LiqMix instrument parameters employed for the generation of BTEX gas standards for the active sampling/solvent extraction method.

After gas standard loading, the front and back sorbent sections of the sampler tube were each placed in separate 2 mL GC vials. The glass wool plug was placed in the vial containing the front sorbent section. 1.0 mL of analytical grade carbon disulfide (CS_2) was added to each vial, as well as 5 µL of 20.500 mg/L deuterated toluene internal standard (prepared from a 99 % Sigma-Aldrich toluene-d8 standard). The vials were then closed tightly with screw caps and the samples were extracted by ultrasonication (Celsius Scientific, South Africa) for 30 min. The organic solution in the vial was separated from the sorbent and was placed in an empty GC vial. 1.0 mL of CS_2 was then added to the sorbent vial, which was extracted again in the same manner. The combined extracts were analysed by GC–MS for which the conditions were the same as for the *in situ* analyses, with the addition of a 3.70 min solvent delay step. The injection volume was 1 µL.

Carbon-based sorbent tubes for thermal desorption

For the preparation of sorbent tubes for thermal desorption, Radiello® graphitized carbon adsorbent cartridges were used (code RAD145, 4.8 mm diameter, packed with 350 ± 10 mg of 35 - 50 mesh Carbograph 4). The cartridges were inserted into empty thermal desorption tubes (Markes, United Kingdom). As these cartridges do not contain secondary traps for capture of any breakthrough, an

Table 5
LiqMix parameters for generation of BTEX gas standards on sorbent tubes for thermal desorption.

Parameter	Value (BT)	Value (EX)
Channel 1 BTEX Standard (g/h)	0.486	1.004
Channel 2 Air/N_2 (NmL/min)	556.2	1168.4
Output 1st stage Air/N_2 (NmL/min)	49.6	261.0
Dilution 2nd stage Air/N_2 (NmL/min)	950.4	897.6
Total Flow (NmL/min)	1000	1159
Batch 1 vaporization at 35 °C		
Benzene (nL/L)	25	-
Toluene (nL/L)	21	-
Batch 2 vaporization at 60 °C		
Ethylbenzene (nL/L)	-	100
o-Xylene (nL/L)	-	100

Note: BT refers to benzene and toluene and EX refers to ethylbenzene and o-xylene.

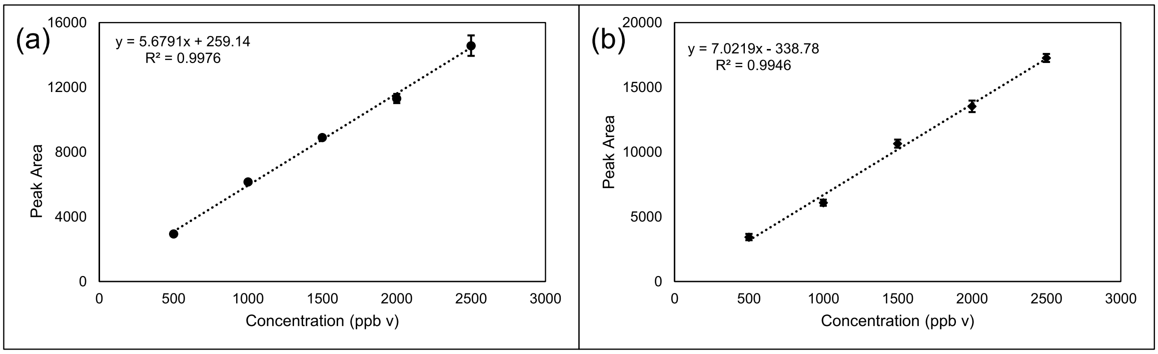

Fig. 4. Linear calibration curves for (a) benzene and (b) toluene obtained from direct injection of the gas standards from the LiqMix into the GC–MS ($n = 10$ for 500 and 1000 ppbv standards, and $n = 5$ for 1500, 2000 and 2500 ppbv standards), with error bars showing the experimental standard deviation. LiqMix experiment conducted at 35 °C.

identical secondary cartridge housed in a thermal desorption tube was connected in series in the sampling train (Fig. 3). The gas flow from the LiqMix was maintained at 60 mL/min using the needle valve to mimic passive VOC sampling conditions. The LiqMix instrument parameters are shown in Table 5. Subsequent to sampling, the tubes were thermally desorbed at a flow rate of 150 mL/min using a TD20 thermal desorption system (Shimadzu, Japan) onto a Tenax® trap prior to desorption onto the GC column by ballistic heating at 50 °C/min to 310 °C using a split of 100:1. Analyses were conducted using a GC coupled to a quadrupole MS (MS-QP 2010 SE, Shimadzu, Japan). The GC–MS parameters were kept the same as with the *in situ* analyses. As with the solvent extraction samples, the secondary cartridges were also analysed to determine if any breakthrough occurred during sampling.

The adsorbed masses were determined from the ideal gas law (Eq. (1)) using Eq. (2):

$$PV = nRT \tag{1}$$

Where;

P – Pressure (Pa)
V – Volume (m^3)
n – Moles (mol)
R – Ideal gas constant ($J.mol^{-1}.K^{-1}$)
T – Temperature (K)

Equation (1) can be re-written as:

$$m = \frac{PVM}{RT} \tag{2}$$

Where;

m – mass (g)
M – molar mass (g/mol)

Quantification was achieved by applying a linear regression model to the results of the analysis of BTEX calibration standards

Table 6
Benzene and toluene GC–MS responses for direct injection of gas standards from the LiqMix.

Concentration (ppbv)	Number of replicates	Benzene		Toluene	
		Peak area	%RSD	Peak area	%RSD
500	10	2949	2.8	3435	7.0
1000	10	6160	1.1	6086	3.8
1500	5	8899	0.3	10,650	2.9
2000	5	11,306	2.5	13,530	3.3
2500	5	14,574	1.3	17,267	1.3

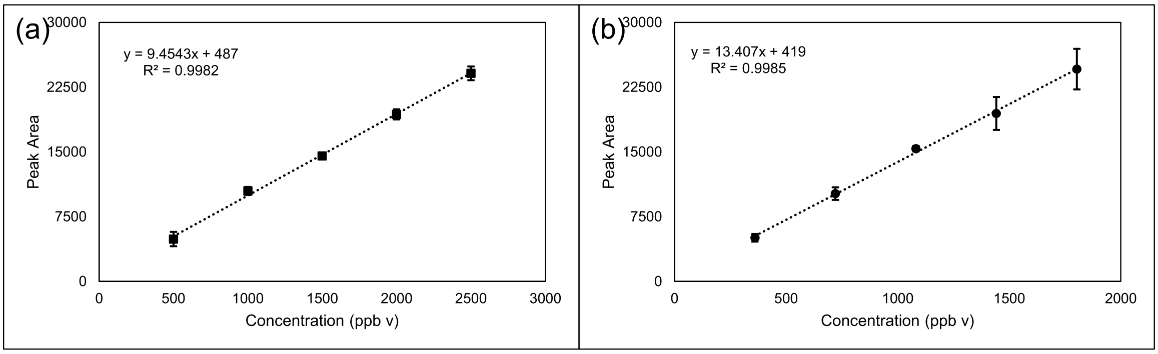

Fig. 5. Linear calibration curve for (a) ethylbenzene and (b) o-xylene obtained from direct injection of the gas standards from the LiqMix into the GC–MS ($n = 10$ for 500 and 1000 ppbv standards, and $n = 5$ for 1500, 2000 and 2500 ppbv standards), with error bars showing the experimental standard deviation. LiqMix experiment conducted at 60 °C.

Table 7
Ethylbenzene and o-xylene GC–MS responses for direct injection of gas standards from the LiqMix.

Concentration (ppbv)	Number of replicates	Ethylbenzene		o-Xylene	
		Peak area	%RSD	Peak area	%RSD
500	10	4899	17	5051	10
1000	10	10,472	4.2	10,167	7.1
1500	5	14,524	2.4	15,371	0.6
2000	5	19,348	3.0	19,448	4.5
2500	5	24,096	1.3	24,589	0.6

prepared from the LiqMix Cascade gas mix instrument that had been adsorbed onto Radiello® cartridges. For the solvent extraction method, the solvent made up the bulk of the sample, thus the detector was switched off at the beginning of the analyses to allow the solvent to elute without overloading the detector and running the risk of shortening its life span.

Trueness tests were conducted by comparing the gas phase BTEX standard generated by the LiqMix with a certified reference material (CRM) BTEX standard (Catalogue No: 30,213, Lot No A0169100, Restek, United Kingdom), containing 4000 µg BTEX solution in a 2 mL vial. 4000 µg of BTEX in the gas phase was thus adsorbed onto the carbon tubes from the LiqMix and desorbed into 2 mL of CS_2 for comparison purposes.

Method validation

Repeatability and reproducibility of the LiqMix cascade

The LiqMix was connected directly to the GC–MS inlet port and through the LiqMix software interface, the desired concentrations of the generated BTEX gas phase standards were selected. These initial tests were conducted at higher concentrations to first establish the optimal settings of the LiqMix and to assess the repeatability and reproducibility of the system prior to the introduction of further dilution for the generation of gas standards for environmental monitoring applications. The linear output of concentrations over a combined range of 500 – 2500 ppbv for benzene and 420 – 2098 ppbv for toluene, yielded R^2 values of 0.9976 and 0.9946 respectively (Fig. 4), with an average percent relative standard deviation (%RSD) of 1.6 and 3.7 % respectively (Table 6).

The linear output of concentrations over a combined range of 365 – 1826 ppbv for ethylbenzene and 361 – 1826 ppbv for toluene, yielded R^2 values of 0.9982 and 0.9985 respectively (Fig. 5), with an average %RSD of 5.6 and 4.65 % respectively (Table 7). Both experiments, namely at 35 °C for benzene and toluene standards, and at 60 °C for ethylbenzene and o-xylene, showed good

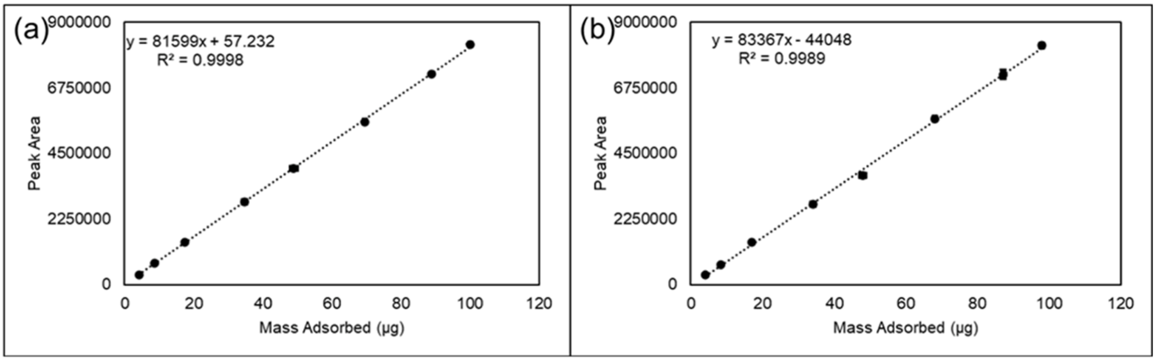

Fig. 6. Linear calibration curves for (a) benzene and (b) toluene from the GC–MS analysis of gas phase BTEX standards adsorbed onto CSC tubes after liquid desorption ($n = 3$), with error bars showing the experimental standard deviation. LiqMix experiment conducted at 35 °C.

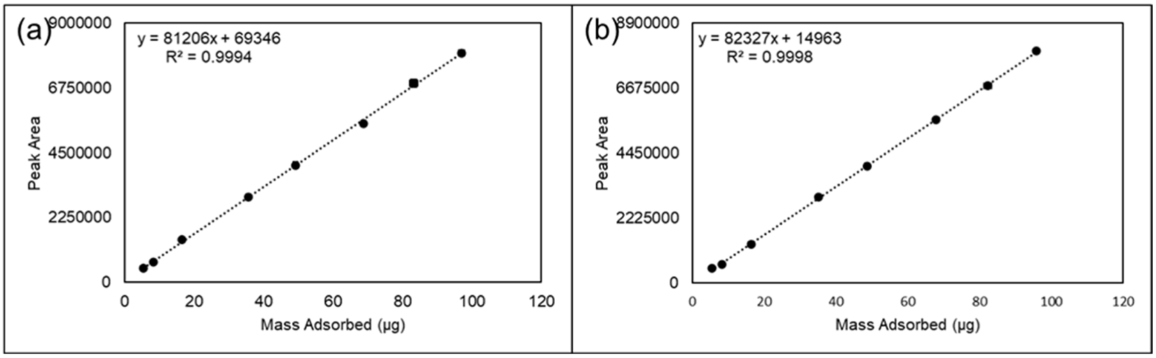

Fig. 7. Linear calibration curves for (a) ethylbenzene and (b) o-xylene from the GC–MS analysis of gas phase BTEX standards adsorbed onto CSC tubes after liquid desorption ($n = 3$), with error bars showing the experimental standard deviation. LiqMix experiment conducted at 60 °C.

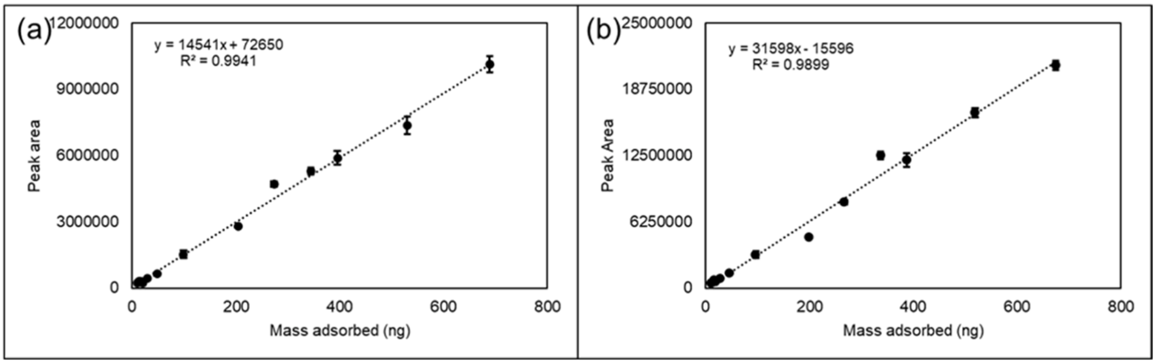

Fig. 8. Linear calibration curves for (a) benzene and (b) toluene from the GC–MS analysis of gas phase BTEX standards adsorbed onto Radiello® cartridges after thermal desorption ($n = 3$), with error bars showing the experimental standard deviation. LiqMix experiment conducted at 35 °C.

repeatability and reproducibility. Higher %RSD values were observed for the 500 ppbv standards in these *in-situ* experiments. Unlike in the adsorption experiments which follow, no preconcentration step was included in the *in-situ* experiments, thus lower concentrations produced smaller signals which are more susceptible to background noise. As the signal approaches noise levels, variability increases, leading to increased %RSD.

Gas phase BTEX standards loaded onto sorbent tubes

The optimised operational parameters were then employed with additional dilution to generate mass loadings in the range of 4 – 100 µg for benzene and 4 – 98 µg for toluene which were adsorbed onto the CSC tubes at 35 °C. The linearity output over these

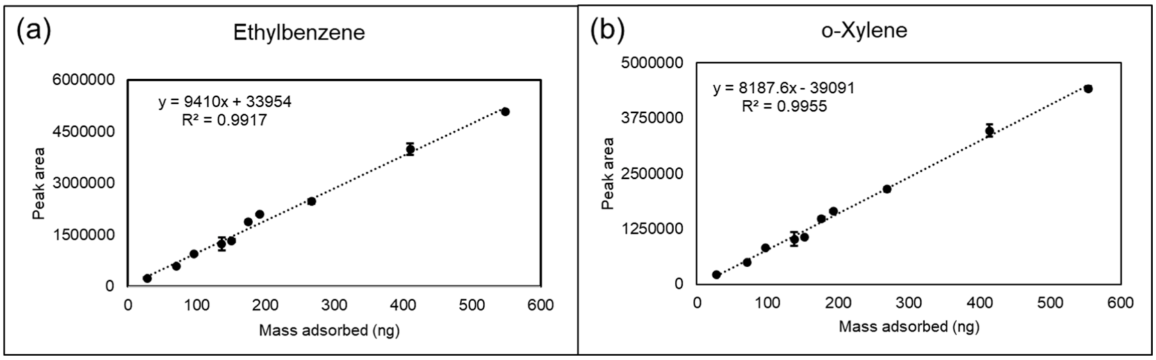

Fig. 9. Linear calibration curves for (a) ethylbenzene and (b) o-xylene from the GC–MS analysis of gas phase BTEX standards adsorbed onto the Radiello® cartridges after thermal desorption ($n = 3$), with error bars showing the experimental standard deviation. LiqMix experiment conducted at 60 °C.

Table 8

Trueness test of the BTEX gas standard prepared from the LiqMix Cascade (LQ-STD) against a certified reference BTEX standard.

Analyte	Sample	Test 1	Test 2	Test 3	Test 4	Test 5	Mean	Std Dev	%RSD
Benzene	CRM (mg/L)	2016	2022	1996	2031	2021	2017	13.07	0.7
	LQ-STD (mg/L)	1991	2027	2016	1991	2026	2011	18.07	0.9
	% difference	1.2	0.3	1.0	2.0	0.2	1.0	0.7	1.2
Toluene	CRM (mg/L)	2016	2021	2034	2012	2016	2020	8.623	0.4
	LQ-STD (mg/L)	2018	2007	2055	2006	2021	2022	19.95	1.0
	% difference	0.1	0.7	1.1	0.3	0.3	0.5	0.4	0.7
Ethylbenzene	CRM (mg/L)	2029	2035	2032	2040	2032	2033	4.159	0.2
	LQ-STD (mg/L)	2020	2029	2040	2032	2033	2031	7.293	0.4
	% difference	0.4	0.3	0.4	0.4	0.1	0.3	0.1	0.3
o-Xylene	CRM (mg/L)	2002	2008	2015	1993	1998	2003	8.546	0.4
	LQ-STD (mg/L)	1971	1977	2012	1962	2023	1989	26.88	1.4
	% difference	1.5	1.5	0.2	1.5	1.3	1.2	0.6	1.3

concentrations was 0.9998 for benzene and 0.9989 for toluene, as shown in Fig. 6, with a %RSD of 1.46 % for both benzene and toluene. For ethylbenzene and o-xylene, the linearity output achieved was 0.9994 and 0.9998 (Fig. 7) when loaded at 60 °C, with a % RSD of 1.39 % for both these analytes, over mass loading in the range 5 - 97 µg and 5 – 96 µg for ethylbenzene and o-xylene respectively.

The calibration employing Radiello® cartridges also showed strong linearity for BTEX compounds, with R^2 values of 0.9941 for benzene, 0.9899 for toluene, 0.9917 for ethylbenzene and 0.9955 for o-xylene, respectively (Figs. 8 and 9). The %RSDs were also low at 3.39 and 3.17 % for benzene and toluene respectively, and 4.17 % for both ethylbenzene as well as o-xylene. These were achieved over mass loading ranges of 10 – 690 ng and 10 – 675 ng for benzene and toluene, and 28 - 548 ng and 28 – 554 ng, for ethylbenzene and o-xylene respectively.

Both analytical methods, namely solvent extraction and thermal desorption, yielded strong linearity. The thermal desorption method tested the LiqMix Cascade at lower levels of BTEXs, where the solvent extraction method is not an ideal method for analysis due to dilution of the sample. This shows that the LiqMix system can be successfully used to calibrate BTEXs at occupational as well as at ambient levels.

Certified reference material

Calibrations obtained for gas standards loaded onto sorbents with subsequent liquid extraction or thermal desorption showed strong linearity over a wide range of concentrations with precise repeatability and reproducibility, however, at this stage the precision and accuracy of the LiqMix still needed to be tested. This was achieved by conducting trueness tests by comparing a 2000 mg/mL BTEX CRM against the BTEX standard produced by the LiqMix Cascade. The results showed a strong similarity between the amount determined for the gas phase BTEX standard and that for the CRM, with a match of 99 % on average (Table 8).

Limitations

The BTEX components have different vapor pressures, with benzene having a vapor pressure of 0.112 atm, toluene 0.037 atm, and ethylbenzene and o-xylene 0.009 atm [7]. These differences in vapor pressure proved to be a challenge when producing the gas phase BTEX standards, since the LiqMix produces these by vaporizing the liquid phase standards. This challenge was highlighted by the poor

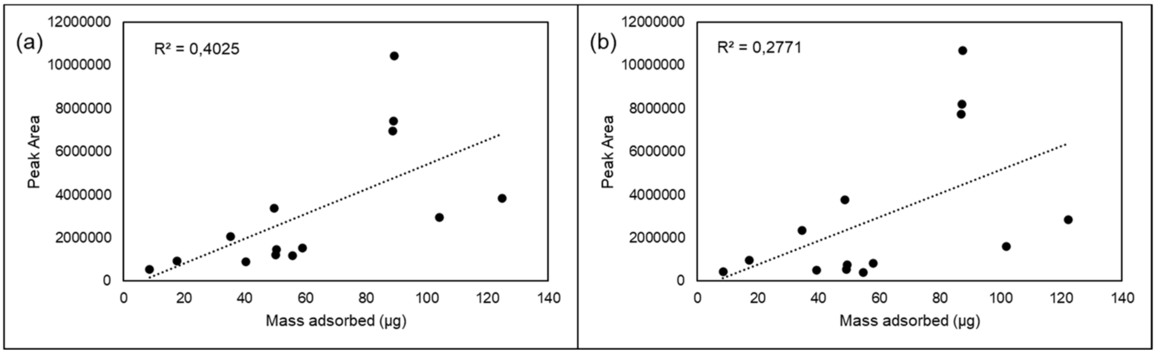

Fig. 10. BTEX calibration curves for (a) benzene and (b) toluene from the GC–MS analysis of BTEX gas standards adsorbed onto CSC tubes after liquid desorption. LiqMix experiment conducted at 60 °C.

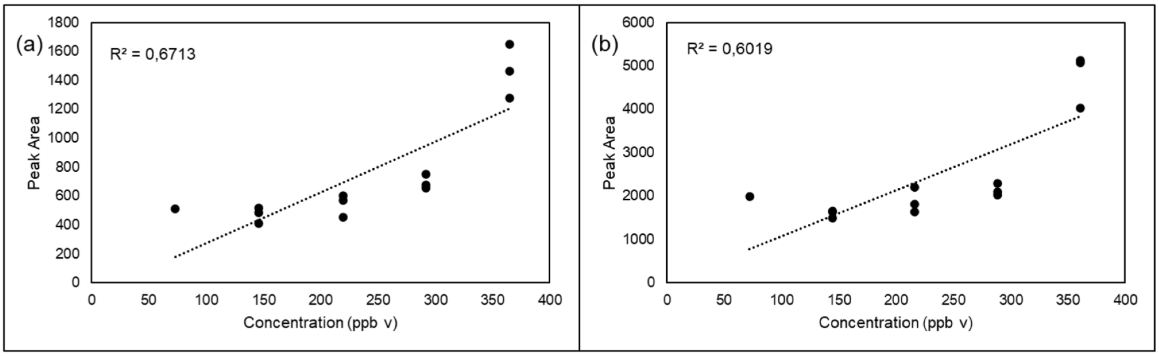

Fig. 11. BTEX calibration curves for (a) ethylbenzene and (b) o-xylene from the direct GC–MS analysis of LiqMix generated BTEX gas standards. LiqMix experiments conducted at 35 °C.

linearity achieved for benzene and toluene when operating the LiqMix at 60 °C, which is the recommended operating temperature, yielding R^2 values of 0.4025 and 0.2771 respectively, as shown in Fig. 10. However, poor linearity was also observed for ethylbenzene and o-xylene when the LiqMix was operated at 35 °C, yielding R^2 values of 0.6713 for ethylbenzene and 0.6019 for o-xylene as shown in Fig. 11. For this reason, benzene and toluene standards were produced when operating the LiqMix at 35 °C, whilst it was operated at 60 °C for ethylbenzene and o-xylene standards, which thus overcame this challenge.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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