Simple and accurate quantification of BTEX in ambient air by SPME and GC-MS

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Abstract

Benzene, toluene, ethylbenzene and xylenes (BTEX) comprise one of the most ubiquitous and hazardous groups of ambient air pollutants of concern. Application of standard analytical methods

for quantification of BTEX is limited by the complexity of sampling and sample preparation equipment, and budget requirements. Methods based on SPME represent simpler alternative, but still require complex calibration procedures. The objective of this research was to develop a simpler, low-budget, and accurate method for quantification of BTEX in ambient air based on SPME and GC-MS. Standard 20-mL headspace vials were used for field air sampling and calibration. To avoid challenges with obtaining and working with required 'zero' air, slope factors of external standard calibration were determined using standard addition and an inherently polluted lab air. For polydimethylsiloxane (PDMS) fiber, differences between slope factors of calibration plots obtained using lab and outdoor air were below 14%. PDMS fiber provided higher precision during calibration while the use of Carboxen/PDMS fiber resulted in lower detection limits for benzene and toluene. To provide sufficient accuracy, the use of 20 mL vials requires triplicate sampling and analysis. The method was successfully applied for analysis of 108 ambient air samples from Almaty, Kazakhstan. Average concentrations of benzene, toluene, ethylbenzene and *o*-xylene were 53, 57, 11 and 14 $\mu\text{g m}^{-3}$, respectively. The developed method can be modified for further quantification of a wider range of volatile organic compounds in air. In addition, the new method is amenable to automation.

Keywords: solid-phase microextraction; GC-MS; standard addition; BTEX; ambient air pollution; air analysis.

1. Introduction

According to the World Health Organization (WHO), in 2012, outdoor air pollution was responsible for the death of 3.7 million people under the age of 60, 90% of whom lived in developing countries [1]. Within hazardous volatile organic compounds (VOCs), special attention is placed on benzene, toluene, ethylbenzene and *o*-, *p*- and *m*-xylenes (BTEX) emitted to the

atmosphere from both anthropogenic and biogenic sources [2]. BTEX pose a serious threat to human health [3], with benzene as a known carcinogen [4,5].

Standard approaches currently used for quantification of BTEX [6–8] are primarily based on trapping analytes onto sorbent tubes followed by thermal desorption, cryogenic focusing and analysis by gas chromatography (GC). Despite of good reliability, these techniques are quite complex, labor and time intensive, and require additional (often expensive) sampling and sample preparation equipment. This significantly limits the capabilities for air monitoring in many developing countries having serious air quality problems.

Compared to standard methods, solid-phase microextraction (SPME) [9–11] constitutes an attractive alternative technique for screening and quantification of VOCs in air. It is based on a passive extraction of VOCs by a thin polymer coating followed by desorption of analytes in a GC injection port. The use of SPME does not require a canister interface or a thermal desorption unit, which are needed for standard methods. Desorption of VOCs from SPME is rapid; it does not require cryogenic focusing and can be automated.

Available SPME-based methods for quantification of VOCs in ambient and indoor air (summarized in Table 1) are based on the following few approaches:

- exposing a fiber to a whole analyzed air;
- exposing a fiber to air sample captured inside a sampling bag or a calibrated bulb;
- time-weighted extraction of air by the fiber retracted inside a protecting needle.

Table 1. Comparison of relevant SPME-based methods for determination of VOCs in ambient air

Authors	Calibration standards preparation	Sampling and sample preparation procedure	Advantages	Disadvantages
Chai and Pawliszyn, 1995 [12]	Spiking standards dissolved in dichloromethane to a 1-L calibrated bulb	Sampling to 6-L canisters, purging the sampled air via the bulb	1) Simple calibration 2) High accuracy of a calibrated	1) Thorough bulb cleaning is required 2) High-purity helium is required

Chai and Tang, 1998 [13]	filled with a pure helium		bulb volume	3) Only manual calibration is possible 4) Limited number of samples may be analyzed due to high cost and mass of canisters
Hippelein, 2006 [14]	Spiking 60 µL of standards dissolved in methanol to gas sampling bags (volume and matrix composition of calibration sample is unknown)	10-min fiber exposure to the analyzed air	1) Simple calibration 2) Ideal for on-site measurements	1) Sampling volumes during calibration and extraction are different and may affect response of analytes 2) Fiber may extract/desorb analytes during transportation 3) High cost of fibers due to single use per sample collection
Martos and Pawliszyn, 1997 [15] Koziel and Pawliszyn, 2001 [16] Tuduri et al., 2001 [17] Tumbiolo et al., 2004 [18] Tumbiolo et al., 2005 [19]	Supplying mixture of pure analytes at a known rate to a known flow rate of air – standard gas generation system.	Fiber exposure at the analyzed air	1) Closest to real conditions calibration – highest accuracy may be achieved 2) Low detection limits	1) 'Zero' air is required 2) Complex standard gas generation system is required 3) Fiber may extract/desorb analytes during transportation 4) High cost of fibers due to single use per sample collection
This study	Spiking standards dissolved in methanol to 20-mL vials filled with lab (non-‘zero’, contaminated) air	Sampling to three replicate 20-mL vials stored in 1 L jars filled with a sampled air	1) Automatic calibration and analysis of samples is possible 2) Simple, robust and low-cost approach	1) Potential in-vial transformation of analytes 2) Special care must be taken to avoid sample leaks via septa

In spite of the high efficiency of all three approaches, they require labor intensive calibration and still have a limited applicability to real ambient air monitoring, which involve analyses of a large number of samples. Controlling the boundary layer around SPME fiber, which impacts extraction rate, can limit the direct use of SPME in the field. Time-weighted average SPME with retracted fiber addresses the control of the boundary layer, but can still be associated with insufficient accuracy due to temperature fluctuations during sampling and adsorption of analytes onto metallic parts of the fiber attachment [20]. Consequently, only few applications of SPME dealing with real air monitoring and representing analysis of a low number of samples have been published. Thus, there is a need for a simple and accurate analytical method utilizing SPME for quantification of volatile air pollutants, so the SPME could have a greater adoption in air quality studies. Specifically, greater adoption of SPME will help minimizing the requirement for (or elimination of) specialized air sampling, sample preparation and sample introduction equipment.

The objective of this research was to develop a simple and accurate method for quantification of BTEX in ambient air using SPME and GC-MS. For the method simplification, standard 20-mL headspace vials were used for sampling and calibration (Table 1). To avoid challenges with obtaining and working with required ‘zero’ air, slope factors of external standard calibration were determined using standard addition approach and a laboratory air. The developed method was successfully applied for the analysis of an ambient air in Almaty, the most populated city in Kazakhstan with a highly contaminated air [21].

2. Experimental

2.1 Standards, solvents and SPME fibers

Benzene (99.8%) and toluene (99.8%) were obtained from EKOS-1 LLP (Moscow, Russia). Ethylbenzene (99.0%), and *o*-xylene (99.0%) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Methanol (HPLC grade) was obtained from AppliChem (Darmstadt, Germany). Helium (>99.995%) was purchased from Orenburg-Tehgas (Orenburg, Russia). SPME fibers – 100 μm polydimethylsiloxane (PDMS), 85 μm Carboxen (CAR)/PDMS and 65 μm PDMS/divinylbenzene (DVB), were obtained from Supelco (Bellefonte, PA, USA).

2.2 Vials for air sampling

Prior to experiments, 20 mL crimp-top glass vials (HTA, Brescia, Italy) were washed by distilled water and pre-conditioned at 160 °C for 4 h. Vials were filled with air samples by shaking open vials for ~60 sec to increase air exchange and then leaving them open for 5-15 min. After sampling, vials were crimped by aluminum caps with polytetrafluoroethylene (PTFE)/Silicone septa (SUN-SRi, Rockwood, TN, USA). Crimp-top vials were chosen over screw top vials to minimize sample losses based on preliminary experiments comparing performance of both vial types.

2.3 Preparation of calibration samples

To prepare air samples with different standard additions of analytes, 1.00 μL of standard solutions containing different analytes concentrations were injected to 20 mL vials filled with lab air. Vials were crimped immediately after injection of standards. At such conditions, relative

standard deviations (RSDs) of BTEX masses extracted were consistently below 10% when 100 μm PDMS fiber was used. Increase of injection volume did not result in the decrease of precision as measured by RSDs. The detailed description of the strategy for preparation of calibration samples is given in Supplemental Material (SM).

2.4 Parameters of GC-MS analyses

Analyses were conducted on 7890A/5975C Triple-Axis Detector diffusion pump-based GC-MS equipped with a split/splitless inlet (Agilent, USA) and Combi-PAL (CTC Analytics, Switzerland) autosampler capable of automated SPME. For separation of BTEX, a 30 m $\times$ 0.25 mm HP-INNOWax (Agilent, USA) column with film thickness 0.25 μm was used. The constant flow of He in column was 1 mL min⁻¹. Thermal desorption of analytes from SPME fiber in GC injector was done in a splitless mode at 250 °C using 0.75 mm i.d. liner (Supelco, USA). Oven temperature was programmed from initial 40 °C (held for 3 min) to 150 °C (held for 1.5 min) at the heating rate of 20 °C min⁻¹.

For validation of the proposed calibration approach (Section 3.2.1), a 6890N/5973N diffusion pump-based GC-MS equipped with a split/splitless inlet (Agilent, USA) and Combi-PAL (CTC Analytics, Switzerland) autosampler was used. For separation, a 60 m $\times$ 0.25 mm DB-WAXetr (Agilent, USA) column with film thickness 0.50 μm was used. Oven temperature was programmed from initial 40 °C (held for 1 min) to 160 °C (held for 2 min) at the heating rate of 10 °C min⁻¹.

Temperatures of ion source, quadrupole and MS interface of both instruments were 230, 150 and 250 °C, respectively. Detection was conducted using electron impact ionization at 70 eV in selected ion monitoring (SIM) mode at m/z of 78, 91, 106 and 106 amu for selective detection and quantification of benzene, toluene, ethylbenzene and *o*-xylene, respectively. For quantification of

ethylbenzene and *o*-xylene, m/z 106 was monitored in favor of the more abundant m/z 91 amu due to higher signal-to-noise ratio and lower potential matrix interferences.

2.5 Methodology of experiments

2.5.1 Validation of the proposed calibration approach

Vials were filled with laboratory air ($T = 300$ K) or outside air ($T = 274$ K), spiked with BTEX standards (section 2.2), sealed and placed into the Combi-PAL agitator for further analysis by SPME-GC-MS. SPME from vials containing air samples was conducted at 30 °C for 3 min using both 100 μ m PDMS and 85 μ m CAR/PDMS fibers.

2.5.2 Comparison of the repeatability when using calibrated gas sampling bulb and 20 mL vials.

Prior to air sampling, two 250-mL calibrated gas sampling bulbs (Sigma-Aldrich, St. Louis, MO, USA) were washed by distilled water and pre-conditioned at 160 °C for 4 h. Ambient air samples were collected by pumping at a flow rate of 1 L min^{-1} for 5 min. Sampling to three replicate vials was conducted as described in Section 2.2. All samples were extracted using 100 μ m PDMS fiber at 30 °C for 3 min and analyzed by GC-MS.

2.6 Air sampling and analysis

Samples were collected at six sites located in five different districts (Bostandyk, Auezov, Medeu, Almaly and Turksib) of Almaty city, Kazakhstan [22]. These sites, labeled S1-S6, were chosen in different parts of the city for assessment of average and representative pattern of BTEX in the whole city (Table S1). Samples were taken 1.5-1.8 m above the ground, (i.e., in the inhalation zone for pedestrians), at the distance >15 m from the road traffic. Meteorological parameters such as

temperature, wind speed and humidity of the air (Table S2) were obtained from a publically-available database [23].

Air sampling was done on March 31, April 2 and 4, 2015. Sampling at each location was carried out at 8 a.m. and 8 p.m. Air samples were collected into 20 mL vials in triplicates. Vials were packed into 1-L clean glass jars, sealed and transported to the laboratory (Fig. S1). Concentrations of BTEX inside vials with a ‘clean’ air stored using the proposed approach did not increase over a 12-day period (Fig. S2) proving that this simple and practical strategy works well. Sample vials were removed from jars immediately before the analysis to minimize interferences to BTEX concentrations. All air samples were analyzed within 4 h after collection using 100 μ m PDMS fiber, controlled extraction temperature of 30 °C, and time = 3 min. Outliers among three replicate measurements were detected and discarded from calculations if RSDs were > 30%.

3. Results and Discussion

3.1 Optimization of the method

3.1.1 Development of a simple and practical calibration approach

Presence of BTEX in the air is a common challenge for many air quality laboratories where special air handling and conditioning is not feasible. To overcome the issue of BTEX presence in the indoor air of the lab, calibration plots were obtained by a standard addition method. The advantage of such methodology is that it does not necessarily require knowing true concentrations of analytes in calibration samples because the obtained calibration slope is assumed equal to the slope for external standard calibration. The proposed approach substantially simplifies a calibration process because ‘zero’ air is not required for the calibration.

Obtained calibration plots for BTEX were linear in the whole studied standard addition concentrations range being 20-200 $\mu\text{g m}^{-3}$ for benzene and toluene and 2-20 $\mu\text{g m}^{-3}$ for ethylbenzene and *o*-xylene (Fig. S3) with squared correlation coefficients $R^2 > 0.99$ (Table S3). Selected BTEX concentration ranges are consistent with those needed for studying polluted urban and indoor air. Mean RSDs ranged from 1 to 5%. According to the calibration, concentrations of benzene, toluene, ethylbenzene and *o*-xylene in lab air were 63, 44, 2.0 and 3.0 $\mu\text{g m}^{-3}$, respectively.

3.1.2 Validation of the proposed calibration approach

In-laboratory prepared calibration standards and ambient air samples differ by chemical composition and atmospheric pressure. The goals of this experiment was (1) to compare calibration plots obtained using a laboratory air ($T = 300\text{ K}$) and ambient air ($T = 274\text{ K}$) and (2) estimate potential matrix effect using two different fiber coatings – absorptive PDMS and adsorptive CAR/PDMS. The PDMS/DVB fiber coating was discarded from further consideration because the addition of 1 μL methanol to the analyzed air sample resulted in the >2-fold decrease of BTEX peak areas when this coating was used. It was probably caused by the competition between methanol and analytes for adsorption sites.

For PDMS fiber, slope factors of calibration plots obtained using outdoor air were ~10% higher than those obtained using laboratory air (Table 2) for all analytes. It was probably due to a higher water vapor pressure in a warmer laboratory air and thus lower extraction effectiveness that is in agreement with previously published data [15].

Table 2. Slope factors of calibration plots obtained using lab (T = 300 K) and outdoor (T = 274 K) air, and measured ambient air concentrations

Analyte	Slope factor		Ambient air intercept	Measured ambient air	True ambient air
	Lab air	Ambient air		concentration, $\mu\text{g m}^{-3}$ (recovery, %) using lab air slope	concentration*, $\mu\text{g m}^{-3}$
100 μm PDMS					
Benzene	20±2	22±1	540±100	26.9 (111)	24.2±4.8
Toluene	73±6	79±2	3720±180	51.3 (109)	47.0±2.5
Ethylbenzene	63±2	71±2	686±20	11.0 (113)	9.7±0.4
<i>o</i> -Xylene	106±3	121±1	1280±12	12.1 (114)	10.6±0.2
85 μm CAR/PDMS					
Benzene	550±30	600±30	13600±3400	24.7 (110)	22.5±5.7
Toluene	780±10	750±30	38000±3000	48.6 (95)	50.9±4.3
Ethylbenzene	280±20	270±30	2600±300	9.3 (96)	9.7±1.5
<i>o</i> -Xylene	420±30	380±40	4240±460	10.0 (89)	11.2±1.7

Note: * determined by a standard addition

Responses to analytes using the CAR/PDMS fiber were 3- to 25-fold higher compared to those for PDMS fiber (Table 2). Due to higher extraction effectiveness, the CAR/PDMS fiber coating was less matrix-affected (i.e., the difference of slope factors was within standard deviations). RSDs for the CAR/PDMS fiber coating were 2 to 3 times greater compared to PDMS coating. This is likely caused by the competition between methanol and BTEX for adsorption sites on the porous CAR/PDMS coating.

Both 100 μm PDMS and 85 μm CAR/PDMS coatings provided similar accuracies. The use of 100 μm PDMS resulted in higher precision associated with a better reliability during calibration (i.e., analysis of a lower number of replicate calibration standards is required), and provided detection limits for benzene 5 $\mu\text{g m}^{-3}$ and 2 $\mu\text{g m}^{-3}$ for other analytes (at a signal to noise ratio 5:1), which is sufficient for their quantification at most regulatory levels. At concentration levels below 5 $\mu\text{g m}^{-3}$, accuracies may be insufficient making the CAR/PDMS coating is a better choice. To

improve accuracy, calibration standards may be obtained using outdoor air, which is closer to the temperature and humidity of real samples.

3.1.3 Comparison of extraction from calibrated gas sampling bulbs and 20 mL vials.

Masses extracted from 250 mL glass bulbs were 3%, 17%, 18% and 9% higher than those from 20 mL vials for benzene, toluene, ethylbenzene and o-xylene, respectively (Table S4), due to a higher total mass of analytes present within the greater sample volume. Such relatively small differences may be explained by low analytes pre-concentration factors of 100 μm PDMS fiber coating [17]. Differences in masses extracted from the bulb and vial will not affect accuracy of real air sample analyses because variations in extraction effectiveness will be included into a slope factor of external standard calibration. RSDs for calibrated bulbs were two times lower than those for 20 mL vials. The highest RSD (20%) was observed for benzene in 20 mL vials, most likely, due to small leaks in replicate samples and proximity of concentration to detection limits. Therefore, to achieve sufficient accuracy and reliability using 20 mL vials, at least three replicates for every sample are recommended. The use of common vials is recommended over specialized air sampling bulbs to keep this method simpler and cost effective.

3.2 Application of the developed method for quantification of BTEX in ambient air of Almaty, Kazakhstan

3.2.1 Measured concentrations

The developed method (Fig. 1) was successfully applied for monitoring of BTEX in ambient air in Almaty, Kazakhstan. Mean concentrations (for all 18 air samples at all six locations) of benzene, toluene, ethylbenzene and o-xylene at different sampling periods ranged from 24 to 89, from 32 to 96, from 6 to 23 and from 7 to 32 $\mu\text{g m}^{-3}$, respectively (Table 3). Average concentrations

of benzene, toluene, ethylbenzene and *o*-xylene calculated as a mean of all 108 measurements were 53, 57, 11 and 14 $\mu\text{g m}^{-3}$, respectively.

Fig. 1. Schematic representation of the developed method for simple and accurate quantification of BTEX in ambient air

Table 3. Mean concentrations of BTEX in Almaty ambient air at different time periods

		Concentration $\pm$ Standard Deviation, $\mu\text{g m}^{-3}$									
Time of sampling >		8:00 a.m.			8:00 p.m.			Daily			All
Date of sampling >		March 31	April 2	April 4	March 31	April 2	April 4	March 31	April 2	April 4	
Benzene	Mean	85 $\pm$ 23	89 $\pm$ 73	26 $\pm$ 10	63 $\pm$ 17	33 $\pm$ 10	24 $\pm$ 3	74 $\pm$ 23	61 $\pm$ 58	25 $\pm$ 7	53 $\pm$ 41
	Max	122	237	37	88	51	27	122	237	43	237
	Min	58	46	17	43	21	20	43	23	17	17
Toluene	Mean	43 $\pm$ 22	96 $\pm$ 195	46 $\pm$ 30	59 $\pm$ 41	62 $\pm$ 32	32 $\pm$ 13	51 $\pm$ 33	79 $\pm$ 134	39 $\pm$ 23	56 $\pm$ 80
	Max	82	494	98	133	100	55	133	494	98	494
	Min	26	10	24	18	22	19	18	10	19	10
Ethylbenzene	Mean	8 $\pm$ 3	23 $\pm$ 42	10 $\pm$ 8	13 $\pm$ 8	10 $\pm$ 4	6 $\pm$ 1	10 $\pm$ 7	16 $\pm$ 30	7 $\pm$ 4	11 $\pm$ 17
	Max	13	108	20	27	17	7	27	107	20	107
	Min	6	4	5	4	4	5	4	4	5	4
<i>o</i> -Xylene	Mean	9 $\pm$ 4	32 $\pm$ 66	10 $\pm$ 8	15 $\pm$ 10	13 $\pm$ 7	7 $\pm$ 2	12 $\pm$ 8	22 $\pm$ 46	8 $\pm$ 6	14 $\pm$ 27
	Max	15	166	24	31	22	9	31	166	24	166
	Min	6	3	5	3	4	4	3	3	4	3

RSDs of triplicate ambient air measurements did not exceed 25% with most replicates being in the range of 10%, which is excellent and sufficient considering the simplicity of the approach for sampling of ambient air. Over the whole study, only twelve ‘outliers’ were detected (<11% of total samples), likely caused by leak from improperly crimped vials.

Concentrations of BTEX in Almaty, Kazakhstan are within the range of reported concentrations of BTEX in cities with major air quality problems such as New Delhi, Cairo, Rome, Ho Chi Minh City, Sao Paulo, or Manila (Table S5) where vehicle exhausts are the main sources of

BTEX, similarly to earlier reports from Almaty [21,24]. The main difference of Almaty from these cities is a colder climate requiring heavy use of heating system in October-April. In Almaty, a substantial part of annual air pollution (about 20%) originates from emissions of power plants and private residential heating systems [21].

3.2.2 Identification of BTEX emission sources

Toluene-to-benzene concentrations (T/B) ratio in ambient air depends on the main source of air pollution, distance from the source and environmental conditions [4,25,26], thus the T/B ratio can be useful for source apportionment studies. The T/B ratio in the studied air samples increased with increasing temperature of a sampled air (Fig. S4), however, linearity of the plot is assumed for simplicity with no evidence for the actual type of relation. Five measurements provided T/B ratios greater than 2 with the highest T/B ratio (3.4) observed in Turksib district. At sub 0 °C sampling temperatures, T/B ratios were below 1.0 in 15 out of 18 samples. Such ratios may indicate that significant fractions of BTEX at the time of sampling originated from non-traffic related sources [27,28]. At lower temperatures, main sources of BTEX are most likely originating from power plants and residential heating, most of which still use coal as a fuel. On Saturday evening, the T/B ratio was close to 1.0 in 50% of sampling locations because the volume of traffic on weekends is much lower than that of weekdays.

4. Conclusions

A simple method for quantification of BTEX concentrations in ambient air was developed utilizing standard, cost effective crimp-top 20-mL headspace vials for air sampling in the field, SPME for headspace extractions, and GC-MS for analyses. For quantification of BTEX, external standard method was used, however, slope factors of calibration plots were determined by a

standard addition method, which did not require a 'zero' air. Transportation and storage of samples in an additional low-cost 1 L sealed glass jars minimized the effects of sample leaks.

Slope factors of calibration plots obtained with a high moisture content lab air ($T = 300\text{ K}$, $RH=70-80\%$) were 9-14% lower than those obtained with a cooler and drier outdoor ($T = 274\text{ K}$) air, probably, due to the effect of water vapor pressure on the extraction effectiveness by the $100\text{ }\mu\text{m}$ PDMS fiber. Use of the CAR/PDMS fiber coating was associated with RSDs being 2 to 3 times higher than the values observed using the PDMS coating, likely due to the more pronounced competition for adsorption sites present on the CAR/PDMS fiber between the analytes and the methanol used as the solvent for spiked standards.

Compared to calibrated 250 mL gas sampling bulbs, 20 mL headspace vials provided 2 times higher RSDs reaching 20% for benzene, however, the sufficient accuracy was achieved by collecting and analyzing triplicate samples. The use of 20 mL vials allows automation of calibration and analysis, which makes it possible to collect and analyze a larger number of samples.

This method was successfully applied for the analysis of 108 ambient air samples taken at six different time periods and six locations within Almaty, Kazakhstan. The number of samples analyzed daily ($n=36$) using a single GC-MS instrument is greater than any previously reported study for a SPME-based air sampling study. Mean concentrations of benzene, toluene, ethylbenzene and *o*-xylene ranged from 24 to 89, from 32 to 96, from 6 to 23 and from 7 to 32 $\mu\text{g m}^{-3}$, respectively. Mean BTEX concentrations over all locations and sampling periods were 53, 57, 11 and 14 $\mu\text{g m}^{-3}$, respectively. These values are comparable with those in the most polluted cities around the world.

Compared to other available SPME-based methods, the developed method is simpler, faster, more labor and cost efficient, and does not require complex or expensive calibration equipment. This method provides a good alternative for low-budget air quality monitoring for BTEX, and is amenable to the addition of other target VOCs of concern in urban air quality assessment. Sampling

with simple vials presents an opportunity to consider ‘crowd-sourcing’ as a means for even more cost-efficient air quality studies.

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Figure 1

1) Preparation of calibration standards

2) SPME-GC-MS of prepared standards

3) Constructing calibration plots

6) Data processing

$$C = S / \text{Slope}$$

5) SPME-GC-MS of samples

4) Air sampling + transportation

1) Standard addition calibration

2) Sampling

3) SPME-GC-MS