5-11-2015

Quantification of benzene, toluene, ethylbenzene and o-xylene in internal combustion engine exhaust with time-weighted average solid phase microextraction and gas chromatography mass spectrometry

Nassiba Baimatova
Iowa State University

Jacek A. Koziel
Iowa State University, koziel@iastate.edu

Bulat Kenessov
al-Farabi Kazakh National University

Follow this and additional works at: https://lib.dr.iastate.edu/abe_eng_pubs

Part of the Agriculture Commons, Bioresource and Agricultural Engineering Commons, and the Organic Chemistry Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/abe_eng_pubs/911. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Quantification of benzene, toluene, ethylbenzene and o-xylene in internal combustion engine exhaust with time-weighted average solid phase microextraction and gas chromatography mass spectrometry

Abstract
A new and simple method for benzene, toluene, ethylbenzene and o-xylene (BTEX) quantification in vehicle exhaust was developed based on diffusion-controlled extraction onto a retracted solid-phase microextraction (SPME) fiber coating. The rationale was to develop a method based on existing and proven SPME technology that is feasible for field adaptation in developing countries. Passive sampling with SPME fiber retracted into the needle extracted nearly two orders of magnitude less mass (n) compared with exposed fiber (outside of needle) and sampling was in a time weighted-averaging (TWA) mode. Both the sampling time (t) and fiber retraction depth (Z) were adjusted to quantify a wider range of Cgas. Extraction and quantification is conducted in a non-equilibrium mode. Effects of Cgas, t, Z and T were tested. In addition, contribution of n extracted by metallic surfaces of needle assembly without SPME coating was studied. Effects of sample storage time on n loss was studied. Retracted TWA–SPME extractions followed the theoretical model. Extracted n of BTEX was proportional to Cgas, t, Dg, T and inversely proportional to Z. Method detection limits were 1.8, 2.7, 2.1 and 5.2 mg m⁻³ (0.51, 0.83, 0.66 and 1.62 ppm) for BTEX, respectively. The contribution of extraction onto metallic surfaces was reproducible and influenced by Cgas and t and less so by T and by the Z. The new method was applied to measure BTEX in the exhaust gas of a Ford Crown Victoria 1995 and compared with a whole gas and direct injection method.

Keywords
volatile organic compounds, passive gas sampling, engine exhaust, time-weighted average, solid phase microextraction, gas chromatography – mass spectrometry

Disciplines
Agriculture | Bioresource and Agricultural Engineering | Organic Chemistry

Comments
This article is published as Baimatova, Nassiba, Jacek A. Koziel, and Bulat Kenessov. "Quantification of benzene, toluene, ethylbenzene and o-xylene in internal combustion engine exhaust with time-weighted average solid phase microextraction and gas chromatography mass spectrometry." Analytica chimica acta 873 (2015): 38-50. DOI: 10.1016/j.aca.2015.02.062. Posted with permission.
Quantification of benzene, toluene, ethylbenzene and \( o \)-xylene in internal combustion engine exhaust with time-weighted average solid phase microextraction and gas chromatography mass spectrometry

Nassiba Baimatova\(^1\), Jacek A. Koziel\(^2*\), Bulat Kenessov\(^1\)

\(^1\) Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, Almaty, Kazakhstan

\(^2\) Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA, USA

Abstract: A new and simple method for benzene, toluene, ethylbenzene and \( o \)-xylene (BTEX) quantification in vehicle exhaust was developed based on diffusion-controlled extraction onto a retracted solid-phase microextraction (SPME) fiber coating. The rationale was to develop a method based on existing and proven SPME technology that is feasible for field adaptation in developing countries. Passive sampling with SPME fiber retracted into the needle extracted nearly two orders of magnitude less mass (\( n \)) compared with exposed fiber (outside of needle) and sampling was in a time weighted-averaging (TWA) mode. Both the sampling time (\( t \)) and fiber retraction depth (\( Z \)) were adjusted to quantify a wider range of \( C_{\text{gas}} \). Extraction and quantification is conducted in a non-equilibrium mode. Effects of \( C_{\text{gas}} \), \( t \), \( Z \) and \( T \) were tested. In addition, contribution of \( n \) extracted by metallic surfaces of needle assembly without SPME coating was studied. Effects of sample storage time on \( n \) loss was studied. Retracted TWA-SPME extractions followed the theoretical model. Extracted \( n \) of BTEX was proportional to \( C_{\text{gas}} \), \( t \), \( D_g \), \( T \) and inversely proportional to \( Z \). Method detection limits were 1.8, 2.7, 2.1 and 5.2 mg m\(^{-3}\) (0.51, 0.83, 0.66 and 1.62 ppm) for BTEX, respectively. The contribution of extraction onto metallic surfaces was reproducible and influenced by \( C_{\text{gas}} \) and \( t \) and less so by \( T \) and by the \( Z \). The new method was applied to measure BTEX in the exhaust gas of a Ford Crown Victoria 1995 and compared with a whole gas and direct injection method.
Keywords: volatile organic compounds, passive gas sampling, engine exhaust, time-weighted average, solid phase microextraction, gas chromatography – mass spectrometry

*Corresponding author:*
Dr. Jacek Koziel, Assoc. Prof.
Air quality engineering and livestock odor
Dept. of Agricultural and Biosystems Engineering
4350 Elings Hall, Iowa State University
Ames, IA 50011, USA
tel. 515-294-4206, fax: 515-294-4250
koziel@iastate.edu

1. Introduction

Air pollution is one of the key environmental problems. It has a significant negative impact on human health and can lead to major socioeconomic losses in terms of quality of life, health care cost and lost productivity. Vehicle exhaust gases are considered as the most dangerous source of ambient air pollution in most cities around the world [1-3]. For example, in the largest city of Kazakhstan, Almaty (~1.5 M inhabitants), vehicle exhausts are responsible for 80% of total air pollutant emissions to ambient air [4]. Estimated total emissions of hydrocarbons, benzo(a)pyrines and benzene are ~24 tons/year [4]. Typical vehicle exhaust gas consist of priority (regulated) air pollutants (SO₂, NO₂, particulate matter, CO), unburned fuel constituents (aromatic and aliphatic hydrocarbons) and their oxidation products (phenols, aldehydes, acids, PAHs). Benzene, toluene, ethylbenzene and xylanes (BTEX) are one of the most toxic constituents of exhaust gases. Toxicity of these compounds is much higher than toxicity of aliphatic hydrocarbons. BTEX can be absorbed by human body through skin or respiratory system [5]. For example, short exposure of benzene on human body leads to drowsiness, headaches and dizziness, long exposure can be a reason of leukemia. [6]. Toluene, ethylbenzene and xylenes negatively affects the central nervous system, disturbed coordination, causes drowsiness, headache [7] and mental disorders [8]. Therefore, knowledge of the concentration levels of BTEX in vehicle exhaust is very important to evaluating contribution of these compounds to air pollution and then to humans health. This data can be used
as an efficient tool to predict the effect of different approaches and technologies for minimization of air pollution caused by BTEX.

Quantification of total emission of BTEX from vehicles requires efficient sampling and analytical method(s). A number of methods have been developed for determination of VOCs concentrations in exhaust gases. The most popular are gas chromatographic methods with different types of sample preparation (dynamic sampling via pumping exhaust through tubes with different types of sorbents [9]), direct sampling with a syringe injection [10], whole air sampling with Tedlar bags [11] and evacuated canisters [12, 13], and solid phase microextraction (SPME) (with exposed fiber) [14]) and detection with mass spectrometric (MS) [15], flame-ionization (FID) [16], infrared [17] methods. These methods often require specialized equipment and interface (e.g., to extract and clean evacuated canisters; pumps, sorbent tubes and thermal desorption) that is cost-prohibitive to many potential users to maintain and to work with. Thus, there is still a need for a simpler method for quantitative analysis of BTEX that can be reliably adapted to multiple and varying applications and be based with a less sophisticated technology and instrumentation (e.g. GC/FID and SPME).

BTEX concentrations and emissions can vary due to the type of engine, age, load, technical integrity of the engine, driving habits, exhaust treatment technology, type of fuel, and many other factors. Thus, it is challenging to evaluate vehicle emissions in a cost-effective manner. Time-weighted averaging (TWA) approach to sampling could be a useful way to ‘even’ out these variations during sampling from a source that is inherently variable (e.g., vehicle exhaust gases). The TWA approach is more precise and much less time and labor consuming. It requires only single event sampling and analysis for a selected time period. Several conventional methods utilize the TWA sampling, pumping sampled gas at a selected flow rate through sorbent tubes or onto whole air canisters (Table 1). Method based on sorbent tubes requires thermal desorber with cryogenic focusing. Pumping the air to a bag or sampling with evacuated canisters is much more simple, but it can be difficult to handle, clean and reuse these devices (Table 1).
Table 1

Comparison of conventional types of methods for quantification of BTEX in gas/air

<table>
<thead>
<tr>
<th>Principle</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active pumping through sorbent tube</td>
<td>Accurate, TWA possible</td>
<td>Pump and thermal desorption system required</td>
</tr>
<tr>
<td>Pumping to air sampling bags; whole air canisters</td>
<td>Simple, accurate, TWA possible</td>
<td>Pump required; difficult to clean and reuse bags</td>
</tr>
<tr>
<td>Direct injection</td>
<td>Simple</td>
<td>Multiple analyses required for TWA</td>
</tr>
<tr>
<td>SPME by exposed fiber</td>
<td>Simple; no pumps required; sampling and sample preparation in one step</td>
<td>Susceptibility to competitive adsorption and compounds displacement. Susceptibility to environmental variables affecting boundary layer around SPME and extraction rate. Particulate matter can introduce interferences</td>
</tr>
<tr>
<td>Passive sampling with retracted SPME (this research)</td>
<td>Simple, TWA possible, reused fiber, fiber can be located directly in exhaust pipe</td>
<td>Complicated calibration and quantification</td>
</tr>
</tbody>
</table>

The objective of this research was to develop a reliable method for quantification of TWA concentrations of BTEX in vehicle exhaust gases using SPME. Specific objectives were to test the efficacy of retracted SPME fiber, i.e., sampling in a mode particularly suited for challenging, moving hot gas stream that is loaded with particulate matter and other potentially interfering compounds. The effects of sampling time, temperature, concentrations, retraction depth, and the contribution of extraction of SPME needle assembly itself were tested. Decision to further investigate the contribution amount of BTEX by the stainless steel of a SPME assembly was driven by early observations of apparent significant, yet very reproducible BTEX mass extracted. Chen and Pawliszyn [18-19] recommended using deactivated SPME needle assemblies (i.e., prototypes that are not commercially available) in order to minimize adsorption of semi-VOCs onto stainless steel, to minimize variations and ensure constant uptake rate in TWA SPME mode. However, such deactivated needles are not available commercially and would be very challenging to assemble. Thus, we aimed at developing a new method that utilizes commercially available SPME fibers.
The rationale was to address the need for a simple (i.e., no special manufacturing process needed for SPME needle deactivation), low-cost, reusable method, amenable for field use and adaptation to various engine exhaust sources and conditions, and not requiring sophisticated sampling and sample preparation technology. Recently commercialized SPME Fast Fit Fiber Assemblies that could be used in diffusive mode are untested and beyond the reach for many scientists in developing countries. Selection of SPME as an alternative approach can provide simpler and more efficient determination of BTEX TWA in exhausts gases (Table 1). In recent decades, SPME developed by Pawliszyn and co-workers [20] as mainly a lab-bench sampling and sample preparation technology. It became very popular due to its simplicity, reusability, being solventless and low cost of operation. Still to date, relatively few attempts were made to bring SPME to the field [21-23]. The TWA SPME approach was used for quantification of toluene in indoor air [18,19], dodecane in indoor air [24], air monitoring of formaldehyde in indoor air [25-27], PAH in creek water [28], n-alkanes in indoor air [29], n-valeraldehyde in air [30], and chlorinated semi-VOCs in landfill gas [31].

To date, there is no method published for quantification of BTEX using TWA SPME approach in hot exhaust gases with the exception of Woolcock et al (2013) [23]. Woolcock et al (2013) [23] have developed a TWA SPME-based method using Carboxen/PDMS fiber coating for quantification of benzene in hot (100 to 125 °C) fast-moving process gases from biomass gasification pilot plant [23]. This research builds on the knowledge gained on quantification of one analyte (benzene) in high temperature, particulate–laden gas phase environment [23]. This approach is developed further for quantification of multiple analytes in vehicle exhaust gases, i.e., an area of application that is of much wider interest and potential application.

2. Theory

SPME can be used for determination of TWA concentrations of VOCs in indoor air [18-22, 24-27, 29, 30]. For this purpose, fiber coating is kept inside protecting needle for a known distance from the needle opening during a prescribed sampling period. The retraction depth serves as a
precisely defined boundary layer that is otherwise not controlled when SPME fiber is exposed to varying convection and turbulence in air or moving gas stream. Extractions rates with retracted SPME fiber are significantly slower and thus, less likely to cause fiber coating overload or analyte displacement. Control of diffusion path is achieved by varying the distance between the tip of SPME fiber and protecting needle opening. Extractions with retracted SPME should follow the Fick’s first law of diffusion. Amount of extracted analyte mass on a retracted fiber coating diffusing from turbulent gas outside though the needle opening with area \(A\) during a sampling time \(t\) is proportional to the diffusion coefficient of the analyte \(D_g\) and its concentration in gas phase \(C_{gas}\) to the diffusion path length \(Z\):

\[
n = \frac{D_g \cdot C_{gas} \cdot t \cdot A}{Z} \quad (1)
\]

where:

\(n\) = mass of compound \(i\) extracted by fiber coating (mg);

\(D_g\) = diffusion coefficient (cm\(^2\) s\(^{-1}\)) for BTEX compound \(i\);

\(t\) = extraction (sampling) time (min);

\(A\) = cross sectional area of SPME needle opening (cm\(^2\));

\(Z\) = diffusion path length (cm).

The gas-phase molecular diffusion coefficient is a physical constant dependent on temperature, pressure and molecule size of analyte. There are several models to estimate diffusion coefficient by gas chromatography [32]. The Fuller, Schettler and Giddings model to estimate the \(D_g\) for binary gas mixture system according its highest method accuracy (3.4%).

\[
D_{AB} = \frac{0.001T^{1.75}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P\left[\left(\sum\nu\right)^{1/3} + \left(\sum\nu_B^{1/3}\right)^{2}\right]} \quad (2)
\]

where:

\(D_{AB}\) = diffusion coefficient for a binary (diluted BTEX compounds in air) system (cm\(^2\) s\(^{-1}\));

\(A, B\) = target BTEX gas molecules;

\(M_A, M_B\) = the molecular masses of solute A (e.g., a BTEX compound, and carrier gas B;
\[ P = \text{gas pressure (atm)}; \]
\[ T = \text{absolute gas temperature (K)}; \]
\[ \sum \nu = \text{molar volumes estimated using contribution method in Table 1 [32].} \]

3. EXPERIMENTAL

3.1 Chemicals

Benzene (99.8% purity), toluene (≥99.9% purity), ethylbenzene (99.8% purity), and \( \text{o-} \) xylene (97% purity) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Ultra-high purity helium (99.99% purity) was obtained from Air Gas (Des Moines, IA, USA).

3.2 SPME

All extractions were completed using a manual SPME holder with 85 µm Carboxen/polydimethylsiloxane (CAR/PDMS) fibers (Supelco, Bellefonte, PA, USA). The choice of SPME fiber type was made based on Chen and Pawliszyn (2003) [19], i.e., because the TWA extraction rates with retracted Carboxen/PDMS fibers are closest to the theory. The manual holder was modified for sampling with retracted SPME fiber according to Koziel and Pawliszyn [27]. Additional notches were milled into the holder Z-slot to retract fiber inside the needle for precisely 5, 10, 15, 20, 25 and 30 mm.

3.3 Gas chromatography-mass spectrometry conditions

All gas samples were analyzed on 6890N/5975C (Agilent, Santa Clara, CA, USA) gas chromatograph with mass selective detector equipped with split/splitless inlet. For separation of BTEX, a 30 m × 0.53 mm BP-20 (SGE Analytical Science, Ringwood, VIC, Australia) column with film thickness 0.50 µm was used. The constant flow of He in column was 7.5 mL min\(^{-1}\). The column flow rate was higher than typical because of a permanent 1 (MS):4 split at the end of the GC column to an olfactometry port (not used for this research). Constant flow to MS was facilitated via 0.15 mm I.D. restrictor. The ion source, quadrupole and MS interface temperatures were 230, 150 and 240 °C, respectively. The GC injection port was working in splitless mode at 250 °C.
Oven temperature was programmed from initial 40 °C (held for 5 min) to 150 °C at the heating rate of 10 °C min\(^{-1}\). Retention times for BTEX were 3.2, 5.2, 7.3 and 8.6 min, respectively. Detection was carried out in SIM mode at m/z\(^{1}\) 78, 91, 106 and 106 for detection and quantification of BTEX, respectively. Total GC run time was 16 min.

3.4 Standard BTEX gas generation system

The standard gas generation system was constructed as shown in Fig.1. The system consisted of linear air pump (Model DDL 8, Gast, Benton Harbor, MI, USA), Model M-30 mini Buck calibrator (A.P. Buck, Inc., Orlando, FL, USA), RM 20 compact low temperature thermostat (Lauda-Brinkmann, LP, NJ, USA), Model 200 syringe pump (KD Scientific, Inc., Holliston, MA, USA), 250 mL flow-through gas sampling bulbs (Sigma-Aldrich, St. Louis, MO, USA), 250 µL gas tight syringe (Hamilton, Reno, NV, USA), HH501 DK thermocouple thermometer (Omega Engineering Inc., Stamford, CT, USA).
Standard gases were used for calibrations of MS detector and for calibration of extractions with retracted SPME fibers. Standard gas generation system was built to deliver flowing gas to simulate dynamic conditions (flowing gas) and temperatures in a tailpipe of engine exhaust. Dynamic gas generation minimizes potential problems with target compound losses due to sorption/desorption onto surfaces [33, 34]. Clean air was pumped into the system and passed through a ‘zero’ air glass bulb for purity check. Specific amounts of BTEX mixture were injected with a motorized syringe pump to a heated port and mixed with pumped air to generate standard gas concentrations. Syringes with ~250 µL of BTEX standard were refilled and exchanged every 10 d. Air-BTEX mixture was then routed through approximately 3 m of PTFE tubing (6 mm O.D.)

Fig. 1. Schematic of dynamic (flowing) BTEX gas standard generation system. Gas samples were collected with retracted SPME fibers from each (n=3) gas bulb.
(Thermo Scientific, Rochester, NY, US) to thermally equilibrate before entering three gas sampling bulbs connected in series with shorter section of the same tubing.

The standard gas system consisted of three gas sampling bulbs to facilitate simultaneous sampling and collection of replicates. Gas sampling bulbs were submerged inside the water bath at 40 °C. All parts of system were cleaned, washed, and baked out in a 150 °C oven overnight before installation. The airflow rate was adjusted with a regulator and confirmed with a flowmeter. Standard gases were extracted with SPME using sampling ports in each glass bulb. Each sampling port was equipped with a Thermogreen half-hole septa for insertion of SPME needle. Target range of BTEX gas concentrations was based on literature and preliminary sampling of engine exhaust. Controlled airflow rate and the rate of BTEX delivery via the motorized syringe pump were used to generate target BTEX concentrations. Theoretical (desired) BTEX concentration for a compound “i” to be generated in the system were calculated according equation (3) [29]:

\[
C_{gas Tài (mass/vol)} = \frac{C_{gas Tài (ppmv)} \cdot P \cdot M_r}{R \cdot T} \quad (3)
\]

where:

- \(C_{gas Tài (ppmv)}\) = theoretical (set point) gas conc. (ppmv) for compound i;
- \(C_{gas Tài (mass/vol)}\) = theoretical (set point) gas conc. (µg m\(^{-3}\)) for compound i;
- \(R\) = ideal gas law constant = 0.008211 atm mol\(^{-1}\) K\(^{-1}\);
- \(T\) = temperature (K);
- \(P\) = pressure (atm);
- \(M_r\) = molecular weight of a BTEX analyte (g mol\(^{-1}\)).

The mass of analyte injected to the standard gas generation system was calculated using equation (4). The BTEX mass injected results from the desired \(C_{gas Tài}\) to be generated, controlled airflow \((Q_{air})\) and the total delivery time \((t)\). The \(t\) was controlled by the syringe pump injection setpoint.

\[
m_{injected} = C_{gas Tài (mass/vol)} \cdot Q_{air} \cdot t_{total} \quad (4)
\]

\(m_{injected}\) = total mass of a BTEX analyte injected by motorized syringe pump (µg);
\( Q_{air} \) = airflow rate (L min\(^{-1}\));

\( C_{gas(mass/vol)} \) = theoretical (set point) gas concentration (\( \mu g \) m\(^{-3}\)) for compound \( i \);

\( t_{total} \) = total delivery time setpoint for the motorized syringe pump (min).

The required total volumes of analytes (\( V \)) for introducing into the system were calculated as a ratio of total mass of BTEX analyte (\( m \)) to their individual densities. The rate of syringe pump was calculated using equation (5):

\[
R_{syringe\ pump} = \frac{V_{total}}{t_{total}} \tag{5}
\]

\[
V_{total} = \sum \left( \frac{m_{injected}}{\rho_i} \right) \tag{6}
\]

where:

\( R_{syringe\ pump} \) = syringe pump delivery rate of BTEX analyte (\( \mu L_{mix} \) min\(^{-1}\));

\( V_{total} \) = total BTEX analyte volume injected to the standard generation system (\( \mu L \));

\( \rho \) = density of compound \( i \) (g mL\(^{-1}\));

\( t_{total} \) = total delivery time setpoint for the motorized syringe pump (min).

Theoretical BTEX \( C_{gas} \) generated in sampling bulbs were adjusted to desired standard concentrations by changing the air flow rate (\( Q_{air} \)) and syringe pump delivery rate. For example, syringe setpoint rate of 0.017 \( \mu L_{mix} \) min\(^{-1}\) and airflow of 500 mL min\(^{-1}\) resulted in 2 ppmv standard \( C_{gas} \) for each BTEX analyte.

### 3.5 TWA BTEX gas sampling with retracted SPME fiber

Gas BTEX TWA sampling with retracted SPME fibers is shown on Fig.2. TWA concentration of BTEX in air flow were estimated by Eq.1. SPME gas sampling rate with retracted SPME fiber (Part A) was controlled by diffusion and retraction depth. Preliminary experiments resulted in a significant (yet reproducible) amounts of analytes extracted by SPME needle assembly. Thus, it became crucial to investigate this apparent uptake of BTEX mass. Part B represents stainless steel fiber attachment wire without SPME coating (a.k.a. “broken” fiber) used to assess the contribution of extraction by SPME needle assembly only.
Fig. 2. SPME gas sampling rate with retracted SPME fiber (Part A) was controlled by diffusion (Eq. 1). Part B represents stainless steel fiber attachment wire without SPME coating (a.k.a. “broken” fiber) was used to assess the contribution of extraction by SPME needle assembly only.

3.6 MS detector calibration with BTEX standard solution

BTEX purity was confirmed by their direct injection to Agilent 6890N/5975C GC-MS. Five mL of MeOH was introduced into a 10 mL vial. Then, 5.7 µL of B, 5.8 µL of T, 5.8 µL of E and 5.7 µL of X were injected into the vial using 10 µL syringe. Concentrations of analytes in the prepared solution made up 1 µg µL⁻¹. On second dilution, a 100 µL of first solution was diluted with 900 µL of MeOH to concentration 100 ng µL⁻¹, and diluted again to concentrations of 0.2, 0.5, 1.0, 1.5 and 2.0 ng µL⁻¹. All prepared samples were analyzed in triplicates by injection of 1 µL in 10:1 split mode at the optimized parameters on GC-MS. Resulting chromatographic peaks were integrated and identified using previously established retention times of single analytes. Detector calibrations were linear in the whole studied concentration range with coefficients of determination $R^2 > 0.99$. Detector response factors (RFs) (i.e., slopes of calibrations) for target analytes and Eq. 7 were used to estimate experimental masses extracted onto SPME using peak area (PA) counts for each BTEX compound:
\[ m = \frac{PA}{RF} \quad (7) \]

3.7 Vehicle exhaust gas sampling

Sampling of BTEX in the exhaust gases was carried out on a 1995 Ford Crown Victoria passenger car with ~230,000 km mileage. Exhaust gas sampling setup consisted of a 102 mm diameter and 1 m length galvanized steel pipe with five gas sampling ports equipped with Thermogreen septa, three of them for simultaneous TWA SPME sampling with three fibers, one – for direct gas sampling with syringe and the last one for measuring temperature of exhaust gases with a digital HH501 DK thermocouple thermometer (Omega Engineering Inc., Stamford, CT, USA). Exhaust gases were sampled using a 10 µL gastight microsyringe followed by direct injection of 1 µL of gas into GC and comparison with SPME-based measurements. Gas TWA SPME sampling time was set to 60 min and 85 µm Car/PDMS fibers were used. Retraction depth \( (Z) \) was 5 mm (Fig. 3).

![Schematic vehicle exhaust gas sampling with retracted SPME fibers in triplicates.](image)

4. Experimental Design

Sampling of generated BTEX gas by SPME was carried out using \( n=3 \) replicate CAR/PDMS fibers. Standard gas flow rate was 0.5 L min\(^{-1}\). SPME conditions (for extraction with exposed and retracted fibers) of all experiments are shown in Table 2. Contribution of mass extracted by “broken” fiber (i.e. stainless steel fiber attachment wire without SPME coating) was subtracted. ‘Experimental’ extracted mass on SPME was estimated using a response factor for MS detector.
and each BTEX compound peak area counts (Eq.7). ‘Theoretical’ mass extracted was estimated using Eq.1 (where \( t, Z \), are experimental extraction conditions and \( C_{gas} \) is the theoretical (set point) BTEX concentrations in the standard gas generation system. \( D_e \) was estimated using Eq.2 and experimental temperature (\( T \)).

### Table 2

Experimental design and ranges of SPME conditions tested.

<table>
<thead>
<tr>
<th>Extraction time, min</th>
<th>Concentration of BTEX, mg m(^{-3})</th>
<th>Diffusion path length Z, mm</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison of gas sampling with exposed and retracted fiber</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 3, 10, 0, 60, 300, 600</td>
<td>7 - 9</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Contribution of extracted mass by needle assembly (a.k.a.)<em>broken</em> fiber</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TWA-SPME verification for gas sampling: effects of ( t, C_{gas}, Z ) and ( T )</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effect of extraction (sampling) time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 3, 10, 0, 60, 300, 600</td>
<td>7 - 9</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>Effect of concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4 - 127</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>Effect of diffusion path length (( Z ))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3, 60, 600</td>
<td>13 – 18</td>
<td>10, 20, 30</td>
<td>313</td>
</tr>
<tr>
<td>Effect of extraction temperature (( T ))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>126 - 170</td>
<td>20</td>
<td>298, 313, 333</td>
</tr>
<tr>
<td>Effect of concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4 - 127</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>Optimization of extraction time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 3, 10, 0, 60, 300, 600</td>
<td>7 - 9</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>Effect of ( Z ) path length</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3, 30, 600</td>
<td>13 - 18</td>
<td>10, 20, 30</td>
<td>313</td>
</tr>
<tr>
<td><strong>Variability associated with SPME</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>5 - 6</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Effect of sample storage time on mass loss</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>5 - 6</td>
<td>20</td>
<td>313</td>
</tr>
<tr>
<td>Storage time – 0, 15, 30, 60 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Storage time – 0, 20, 40, 60 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>BTEX quantification in vehicle exhaust gas</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>336-338</td>
<td></td>
</tr>
</tbody>
</table>

5. Results and discussion
5.1 Comparison of extractions with exposed and retracted fiber

The rate of extraction onto retracted SPME fiber is significantly lower and could be controlled by adjusting time \( t \) (Fig. 4).

- Mass extracted with exposed SPME fiber
- Mass extracted with retracted fiber

**Fig. 4.** Comparison of mass of BTEX extracted with exposed & retracted fibers. Gas sampling completed at diffusion path length \( Z=20 \) mm, \( T=313 \) K, extraction time \( t=1, 3, 10, 30, 60, 300 \) and \( 600 \) min, standard gas flow \( 0.5 \) L min\(^{-1}\), \( C_{gas}(B)=6.7 \) mg m\(^{-3}\), \( C_{gas}(T)=8.1 \) mg m\(^{-3}\), \( C_{gas}(E)=8.5 \) mg m\(^{-3}\), \( C_{gas}(X)=8.6 \) mg m\(^{-3}\).

Exposed fiber extracted ~ 2 to 3 orders of magnitude more BTEX mass compared with retracted fiber over sampling time \( t \) ranging from 1 min to 600 min. However, extraction rate is dependent on variables that are difficult to control in ambient air or gas streams. These variables include air/gas speed and temperature that affect the thickness of the boundary layer around SPME fiber. In addition, competitive adsorption and susceptibility to analyte displacement from SPME was also documented in previous research [22]. Quantification of volatiles with exposed SPME fibers is possible, albeit typically limited to shorter extraction times and careful consideration of affecting
environmental and matrix conditions. Retracted SPME fiber was not affected by SPME coating saturation and SPME behaved as a “zero” sink sorbent. Extracted BTEX mass was proportional to $t$ over the entire tested range allowing continuous and linear extraction that is less susceptible to aforementioned environmental and matrix effects and constraints. Extraction with retracted fiber was much slower because it was controlled by diffusion and was proportional to time-weighted average analyte concentration in the gas stream. Air/gas speed no longer influences the boundary layer conditions. Analyte extractions over much longer time periods are possible while fiber coating is protected from (e.g.) particles and soot in exhaust gas streams.

Mean relative standard deviations (RSDs) of extracted mass also improved, i.e., RSDs decreased from 9, 8, 10 and 8% for exposed fiber to 5, 7, 6 and 4% for retracted fiber and B ($p=0.07$), T ($p=0.69$), E ($p=0.13$), and X ($p=0.04$), respectively. It was also observed that variability of mass extracted with retracted fiber improved when the mass extracted by “broken” fiber (i.e. stainless steel fiber attachment wire without SPME coating) was subtracted. In contrast, the linear extraction range for exposed fiber was limited to <30 min with apparent saturation in ~60 min. The goal of the next experiment was to establish the contribution of “broken” fiber onto BTEX extraction.

5.2 Contribution of extracted mass by needle assembly (a.k.a.) ‘broken’ fiber

The ‘broken’ fiber (i.e., SPME stainless steel assembly without coating) acted like a reliable ‘sampling device’. The contribution by “broken” fiber as a part of total mass extracted was reproducible and was influenced by $t$ and $C_{gas}$ with very small influence of $T$ and $Z$. The lowest RSDs (0.5 to 2.9%) were found for high $C_{gas}$ (>80 mg m$^{-3}$) and the highest RSDs (1.8 to 6.0%) were found at the 25 to 35 mg m$^{-3}$ $C_{gas}$. The mean contribution of ‘broken’ fiber assembly was 13, 29, 50 and 45% for BTEX, respectively, and needs to be considered and controlled for quantitative analysis (Fig. 5).
• Mass extracted with metallic surfaces
• Total mass extracted with SPME retracted fiber

**Fig. 5.** Contribution of mass extracted by needle assembly to the total mass extracted by retracted SPME fiber. Gas sampling time \( (t) = 30 \) min, \( Z = 20 \) mm, \( T = 313 \) K.

The % contribution was directly proportional to \( MW \) and inversely proportional to \( D_g \) and vapor pressure (Fig.6) (see Fig. S1 in Supplemental Materials). Closer inspection of the data showed that the % contribution slightly varied with \( C_{gas} \) in a bimodal trend, i.e., initial increase was followed by decrease that is more apparent as \( M \) increases (see Fig. S2 in Supplemental Materials). This decrease can be caused by saturation of metallic surfaces of a “broken” fiber.
Fig. 6. Effects of MW (part a), $D_g$ (part b) and vapor pressure (part c) on the % of BTEX extracted ratio of broken by fiber coating. $T=40$ °C, $t=30$ min, $C_{gas}$ variable.

Extraction time significantly affected % of BTEX mass extracted by metallic surfaces of assembly (Fig. 7) in a bimodal fashion. Short $t$ (<10 min) were characterized by higher (60±30%) % contribution of metal assembly. It is likely caused by initial extraction and ‘saturation’ of metallic surfaces. After ~30 min extraction, the % contribution was virtually constant (15±10%). RSDs were also higher at shorter $t$ ranging from 71 to 139%. For longer extraction times (>30 min), RSDs are lower (5-96%). These results were consistent with Chen and Pawliszyn [19] (see Fig. S3 in Supplemental Materials)). Thus, it is recommended that (i) a $t > 30$ min gas sampling be used when analyzing car exhaust since the % contribution is stable. Alternatively, (ii) a shorter $t$ could be also used. However, sampling will be more susceptible to variability due to extraction on metallic surfaces. Both $t$ can be useful to quantify BTEX in vehicle exhaust.
Fig. 7. Effects of $t$ on BTEX extraction (sampling vol. = $m/C_{gas}$). $Z=2$ cm, $T=40$ °C.

*Effect of retraction depth Z.* Measured % contribution to extraction by metallic surfaces of fiber assembly ranged from 22 to 48% ($t=3$ min), from 10 to 26% ($t=30$ min) and from 0 to 6% ($t=600$ min), respectively (Fig. S4 in *Supplemental Materials*) and were consistent with sampling rates for the SPME retracted fiber coating. However, the actual effect of $Z$ change was small, i.e., resulting in insignificant change of sampling rate. The increase of $t$ resulted in lower % contribution. Thus, it is recommended to use longer $Z$ to minimize the % contribution by “broken” fiber assembly, similarly to an earlier recommendation based on the effects of $t$ (Fig. S3). Longer $Z$ increases the area of metallic surface of SPME assembly inside protecting needle while the exposure of outside metallic surfaces can be controlled by minimizing the needle exposure outside of the septum (Fig 2).

*Effects of $T$.* Measured % contribution to extraction by metallic surfaces of fiber assembly ranged from 10 to 13%, from 22 to 26%, from 33 to 41%, from 29 to 41% for BTEX, respectively (Fig. S5 in *Supplemental Materials*) and were consistent with sampling rates for the SPME retracted fiber. Higher $T$ increased $D_g$. This, in turn increased the sampling rate both the retracted
fiber and the metallic surfaces. However, the actual effect of $T$ change was small, i.e., resulting in insignificant change of sampling rate (Fig. S5).

Practical means to control the contribution of metallic surfaces to extractions.

Contribution of needle metallic surfaces to the whole extraction process needs to be considered. However, there is an apparent solution to account for it, minimize its contribution, minimize the variability, while operating within the Fick’s law range for the SPME extraction (Fig.8). It is recommended that simultaneous extractions with a retracted “broken” fibers and SPME fibers with all extraction parameters kept identical are made. Then, the contribution of extraction by metallic surfaces can be subtracted from mass extracted by the SPME fiber.

![Diagram](image)

**Fig. 8.** Minimizing variability associated with the % contribution by metallic surfaces of SPME needle assembly.

Alternatively, the use of deactivated metallic surfaces could be considered as proposed by Chen and Pawliszyn, 2003 [19]. This technology has not been commercialized yet and its potential precision and accuracy is not known at this time.

5.3 Variability associated with SPME

Differences in sampling rate between randomly tested Carboxen/PDMS fibers were more apparent when the retracted sampling mode was used (Fig. 9). The RSDs associated with the mean mass extracted in retracted (exposed) mode were 19% (13%), 39% (12%), 46% (12%), 49% (13%) for BTEX, respectively. As expected, mass extracted by exposed fibers (B) were ~ two orders of magnitude greater than mass extracted with by the same fibers used in retracted mode (A).
However, the % difference in mass extracted using n=4 retracted fibers ranged from 67 to 108%, from 39 to 100%, from 29 to 100% and from 26 to 100% for BTEX, respectively. Exposed fiber extraction were more reproducible, yet still the differences were significant and ranged from 61 to 100%, from 62 to 100%, from 66 to 100% and from 67 to 103% for BTEX, respectively. RSDs associated with each of n=4 retracted fibers were similar and ranged from 7 to 8%, from 6 to 9%, from 4 to 5% and from 3 to 6% for fiber #1, 2, 3 and 4, and BTEX, respectively. RSDs associated with each of n=4 exposed fibers were similar and ranged from 4 to 10, from 2 to 8, from 3 to 9 and from 3 to 10% for fiber 1, 2, 3 and 4, and BTEX, respectively. Extraction with retracted SPME fibers can be reasonably modeled with the Fick’s Law (Eq. 1) and fiber type should not influence n. However, Chen and Pawliszyn [19] showed differences in sampling rates for different fiber coatings. Furthermore, fiber coating surface may vary due to the presence of microcracks/chips and wear & tear to metallic surfaces (Fig. S9).

Fig. 9. Variability among n=4 random CAR/PDMS 75 µm fibers on mass extracted with retracted fiber (A) and exposed fiber (B), t= 3 min, Z=20 mm, T=40 °C, $C_{gas}(B)=5.0$ mg m$^{-3}$, $C_{gas}(T)=5.8$ mg m$^{-3}$, $C_{gas}(E)=6.2$ mg m$^{-3}$ and $C_{gas}(X)=5.9$ mg m$^{-3}$.

Such inconsistencies may potentially affect fiber efficiency and rate of extraction. Therefore, it is recommended to either use a carefully selected sets of fibers that perform reasonably similar or use the same SPME fiber for TWA extraction to prevent errors caused by random differences in fiber efficiency. In that former case, separate calibration should be obtained for each fiber.

5.4. Effect of sample storage time on mass loss
Comparison of sample analytes losses from the SPME fibers during storage is shown in Fig 10. Mass loss from fibers used in retracted mode ranged from 4 to 33%, from 7 to 45%, from 11 to 50% and from 13 to 53% for BTEX, respectively (Fig. 10A). Mass loss from fibers used in exposed mode was relatively lower and ranged from 5 to 27%, from 2 to 23.5%, from 1 to 24% and from 1 to 24% for BTEX, respectively (Fig. 10B). Furthermore, analytes extracted by retracted fiber were more susceptible to the faster rate of sample loss, i.e., the fastest mass loss rate was observed at the early stages of storage (Fig. 10A) compared with the same phenomena observed much later for exposed mode samples (Fig. 10B). It is hypothesized that this is caused by lower absolute amount of mass extracted and a potential presence of residual, un-bound, gas-phase analytes inside the needle that can be readily back-diffused/lost outside of needle during storage. Thus, special care must be taken to minimize or account for analytes losses during storage, especially when analyzing real field samples far from the lab [27].

Fig. 10. Comparison of the effect of the sample storage time at room temperature on mass loss with retracted fiber (A) and exposed fiber (B); extraction conditions: \( t = 3 \) min, \( Z = 20 \) mm, \( T = 40 \) ℃, \( C_{gas}(B) = 5.0 \) mg m\(^{-3}\), \( C_{gas}(T) = 5.8 \) mg m\(^{-3}\), \( C_{gas}(E) = 6.2 \) mg m\(^{-3}\) and \( C_{gas}(X) = 5.9 \) mg m\(^{-3}\).

5.5 TWA-SPME verification for gas sampling: effects of \( t, C_{gas}, Z \) and \( T \)

Method verification was completed by comparison experimental (measured) and theoretical (Eq. 1) mass extracted as the function of \( t, C_{gas}, Z \) and \( T \) (Fig. 11 and Table S1). Extractions with retracted fibers followed Fick’s law model (Eq. 1). Subtraction of extracted mass on metallic surfaces of needle assembly generally improves the match. Figure 11 represents comparison of
extracted and theoretical mass for all experiments. The range of measured mass deviation from the theory was -22%, 21%, 65% and 21% for BTEX, respectively. The mean contribution of metallic surfaces was 3%, 16%, 38% and 21% for BTEX, respectively.

Fig. 11. Relationship between theoretical and experimental mass extracted.

Effect of extraction (sampling) time. Mean masses extracted were greater than ‘theoretical’ by 12, 14, 12 and 23% for BTEX, respectively. RSDs varied from 2 to 9%, from 0.1 to 14%, from 1 to 13%, from 1 to 9% for BTEX, respectively. The use of longer sampling times (≥60 min) significantly improved (i.e., from 64 to 38%) matching the theory (Eq. 1). This is also illustrated with improved match of sampling rates in Fig. S3. Thus, the use of longer sampling times is recommended (Fig. 8).
Effect of analyte concentration. Mean massed extracted were higher than “theoretical” by 6, 14, 32 and 15% for BTEX, respectively. RSDs varied from 2 to 15%, from 3 to 15%, from 4 to 15%, from 4 to 18% for BTEX, respectively. Greater RSDs and closer match to theory were observed at the lower range of $C_{gas}$. The mean % difference for (lower range) $C_{gas} < 30$ mg m$^{-3}$ was 5, 4, 21, and 2% for BTEX, respectively. The mean % difference for (higher range) $C_{gas} \geq 30$ mg m$^{-3}$ was 8, 18, 43, and 20% for BTEX, respectively. Calibration plots for BTEX were linear in the whole studied concentration range with $R^2$ > 0.99 (Fig S7). Method detection limits estimated at $p=0.95$ confidence level were 1.6, 2.7, 2.1 and 5.2 mg m$^{-3}$ for BTEX, respectively.

Effect of retraction depth $Z$. The mass and sampling rate was a function of $1/Z$ at extraction times 3, 30, and 600 min (Fig. S4, $R^2$ ranged from 0.83 to 0.99). Percent difference between experimental and theoretical mass was generally lower for $t=30$ min and increased with $Z$, i.e., ranged from 7% for $Z=10$ mm to 30% for 30 mm, from 2% for $Z=10$ mm to 30% for 30 mm, from 5% for $Z=10$ mm to 36% for 30 mm, from 2% for $Z=10$ mm to 36% for 30 mm, for BTEX, respectively. RSDs for mass extracted improved with increasing $t$, i.e., 16-19%, 10-59%, 16-59%, 16-66% for $t=3$ min; 6-14%, 11-16%, 17-30%, 11-27% for $t=30$ min; 6-9%, 8-11%, 6-8%, 7-11% for $t=600$ min and BTEX, respectively.

Effect of temperature. Increase of $T$ led to an increase in the efficiency of analyte extraction (Fig. S5, Table S1). This is increase was likely due to the increase of $D_g$ and it was not apparently affected by lower partitioning to SPME coating with $T$ [20]. Compounds with lower $MW$ were affected by the effects of $T$ more than those with greater $MW$. Experimental mass extracted were greater than “theoretical” by 48, 48, 42, 61% for BTEX, respectively. RSDs ranged from 2-6%, from 3-8%, from 4-10%, from 4-9% for BTEX, respectively.

5.5 BTEX quantification in vehicle exhaust gas

Table 3 shows comparison of measured concentrations of BTEX in exhaust gases determined by TWA-SPME method and by direct injection of grab air sample to GC-MS. The value of DI-based measurement was screening only, i.e., it provided with a quick reference for the
concentration BTEX range and a guide for adjusting $t$ and $Z$. Masses extracted with retracted fibers were adjusted considering the variability of three fibers used for each Trial and the effects of sample losses due to storage. Mass extracted by metallic surfaces of SPME needle assembly were subtracted. Each direct injection sampling data point represents concentration by $n=2$ in field Trial 1 and by $n=3$ in Trial 3.

**Table 3**

Comparison of SPME-TWA with direct gas injection (DI). TWA conditions: temperature of exhaust $T=336-338$ K, $Z=5$ mm, $t=60$ min. DI grab samples collected at $t = 5$ min, 25 min and 45 min.

<table>
<thead>
<tr>
<th></th>
<th>Trial 1</th>
<th></th>
<th></th>
<th>Trial 2</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{gas}$, mg m$^{-3}$</td>
<td>TWA SPME</td>
<td>RSD (%)</td>
<td>DI</td>
<td>RS D (%)</td>
<td>TWA &amp; DI diff., %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n=3</td>
<td>n=2</td>
<td>TWA</td>
<td>n=3</td>
<td>n=3</td>
</tr>
<tr>
<td>B</td>
<td>1.8±0.1</td>
<td>4.1</td>
<td>2.0±1.2</td>
<td>60.8</td>
<td>6.5</td>
<td>0.9</td>
</tr>
<tr>
<td>T</td>
<td>2.9±0.5</td>
<td>15.5</td>
<td>3.9±3.3</td>
<td>84.6</td>
<td>26</td>
<td>0.7</td>
</tr>
<tr>
<td>E</td>
<td>0.5±0.1</td>
<td>16.8</td>
<td>1.1±0.7</td>
<td>67.5</td>
<td>52</td>
<td>0.5</td>
</tr>
<tr>
<td>X</td>
<td>0.6±0.1</td>
<td>16.7</td>
<td>1.8±1.3</td>
<td>72.6</td>
<td>67</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Note: * $C_{gas}$ below method detection limits

RSDs for $C_{gas}$ measured with TWA-SPME (n=3) in Trial 1 were 4, 16, 17 and 17% for BTEX, respectively. RSDs for $C_{gas}$ measured with TWA-SPME (n=3) in Trial were 9, 25, 25 and 19% for BTEX, respectively. RSDs for direct injection sampling points (Trial 1) were understandably greater at 61, 85, 68 and 73% for BTEX respectively. This was likely caused by $C_{gas}$ variations in the exhaust gas. RSDs for direct injection sampling points (Trial 2) were 21 and 53% for benzene and toluene respectively while the ethylbenzene and o-xylene were not detected.

A reasonable, order of magnitude match was found considering inherent differences in both methods. Percent difference between TWA-SPME and DI – based $C_{gas}$ (Trial 1) were 7, 26, 52 and 67% for BTEX respectively. Percent difference between TWA-SPME and DI – based $C_{gas}$
(Trial 2) were 65 and 39% for benzene and toluene respectively. Statistical $t$-test was used for comparison of DI and TWA-SPME sampling at 95% confidence level. $t$-Test statistics (Trial 1) between TWA-SPME and direct injection $C_{gas}$ were 0.9, 0.7, 0.5 and 0.4 for BTEX respectively. $t$-Test statistics (Trial 2) between TWA-SPME and direct injection $C_{gas}$ were 0.03, and 0.14 for B and T, respectively. SIM chromatograms of TWA-SPME sampling of BTEX in exhaust gases with retracted steel needle assembly (without SPME extraction phase) and retracted Carboxen/PDMS SPME fiber are shown in Fig. 12. Extraction on metallic parts contributed 11 to 21% of total BTEX mass extracted. This % contribution was minimized with the choice of $t$ and $Z$ recommended in Fig. 8, i.e. shorter $Z$ and longer $t$ needed for conditions with low $C_{gas}$.

![SIM chromatograms of TWA sampling of BTEX in exhaust gases with retracted steel needle assembly (without SPME extraction phase) and retracted Carboxen/PDMS 85 µm SPME fiber. $Z=5$ mm, $t=60$ min, $T=25$ to 67 °C.](image)

**Fig. 12.** SIM chromatograms of TWA sampling of BTEX in exhaust gases with retracted steel needle assembly (without SPME extraction phase) and retracted Carboxen/PDMS 85 µm SPME fiber. $Z=5$ mm, $t=60$ min, $T=25$ to 67 °C.

**Conclusions**

A new method for quantification of TWA concentrations of BTEX in vehicle exhaust gases using retracted SPME was developed. Efficacy of retracted fiber, i.e., sampling in a mode particularly suited for challenging, moving hot gas streams that are loaded with particulate matter and other potentially interfering compounds was tested in lab and field conditions. The effects of $t$, $T$, $C_{gas}$, $Z$ (fiber retraction depth), and the contribution to extraction by metallic surfaces of the
SPME needle assembly itself were tested. The rationale was to develop a method based on existing and proven SPME technology that will be useful for field adaptation in developing countries. The main findings are as follows:

1. The rate of extraction onto retracted SPME fiber was significantly lower and could be controlled by adjusting $t$ or $Z$. Exposed fiber extracted >100× more BTEX mass compared with retracted fiber over $t$ ranging from 1 min to 600 min. Retracted SPME fiber was not affected by SPME coating saturation and SPME behaved as a “zero” sink sorbent.

2. Extractions with retracted fibers followed Fick’s law model (Eq. 1). Subtraction of extracted mass on metallic surfaces of needle assembly generally improved the match.

3. The ‘broken’ fiber (i.e., metallic surfaces of SPME stainless steel assembly without coating) acted like a reliable ‘sampling device’. The mean contribution was 3%, 16%, 38% and 21% for BTEX, respectively, and needed to be considered and controlled for quantitative analysis. The % contribution was directly proportional to compound $MW$ and inversely proportional to $D_g$ and vapor pressure. It is recommended that (i) a $t > 30$ min gas sampling be used when analyzing car exhaust since the % contribution was stable. Alternatively, (ii) a shorter $t$ could be also used. However, sampling will be more susceptible to variability due to extraction on metallic surfaces. Both $t$’s can be useful to quantify BTEX in vehicle exhaust. It is recommended that simultaneous extractions with a retracted “broken” fibers and SPME fibers with all extraction variables identical are conducted. Then, the contribution of extraction by metallic surfaces can be subtracted from mass extracted by the SPME fiber.

4. It is recommended to either use a carefully selected sets fibers that perform reasonably similar or use the same SPME fiber for TWA extraction to prevent errors caused by random differences in fiber efficiency. In that former case, separate calibration should be obtained for each fiber.

5. BTEX analytes extracted by retracted fiber were more susceptible to the faster rate of sample loss during storage.
6. New method was tested for quantification of BTEX in an idling vehicle exhaust. A reasonable, order of magnitude match with direct gas injection method was found considering inherent differences in both methods.

7. A set of recommendations was developed to minimize and account for the contribution of metallic surfaces that are consistent with recommendations for adjusting the $t$ and $Z$ to accommodate a wide range of vehicle gas exhaust parameters and BTEX concentrations.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This information is available free of charge.

Notes

The authors declare no competing financial interests

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

ACKNOWLEDGEMENTS

Authors are grateful to the Ministry of Education and Science and al-Farabi Kazakh National University for financial support of the Ph.D. project of Nassiba Baimatova and her two research visits to Iowa State University. The work was also supported by the grant of the Ministry of Education and Science 0112PK01391 “Development of methodologies for control of organic environmental contaminants in Kazakhstan using the methods of green analytical chemistry”.

28
References


List of Figures

**Figure 1.** Schematic of dynamic (flowing) BTEX gas standard generation system. Gas samples were collected with retracted SPME fibers from each (n=3) gas bulb.

**Figure 2.** SPME gas sampling rate with retracted SPME fiber (Part A) was controlled by diffusion (Eq. 1). Part B represents stainless steel fiber attachment wire without SPME coating (a.k.a. “broken” fiber) was used to assess the contribution of extraction by SPME needle assembly only.

**Figure 3.** Schematic vehicle exhaust gas sampling with retracted SPME fibers in triplicates.

**Figure 4.** Comparison of mass of BTEX extracted with exposed & retracted fibers. Gas sampling completed at diffusion path length (Z)=20 mm, T= 313 K, extraction time (t)= 1, 3, 10, 30, 60, 300 and 600 min, standard gas flow 0.5 L min⁻¹, \(C_{gas}(B)=6.7\) mg m⁻³, \(C_{gas}(T)=8.1\) mg m⁻³, \(C_{gas}(E)=8.5\) mg m⁻³, \(C_{gas}(X)=8.6\) mg m⁻³.

**Figure 5.** Contribution of mass extracted by needle assembly to the total mass extracted by retracted SPME fiber. Gas sampling time (t)=30 min, Z=20 mm, T=313 K.

**Figure 6.** Effects of MW (part a), \(D_g\) (part b) and vapor pressure (part c) on the % of BTEX extracted ratio of broken by fiber coating. \(T=40\) ºC, \(t=30\) min, \(C_{gas}\) variable.

**Figure 7.** Effects of \(t\) on BTEX extraction (sampling vol. = \(m/C_{gas}\)). Z=2 cm, \(T=40\) ºC.

**Figure 8.** Minimizing variability associated with the % contribution by metallic surfaces of SPME needle assembly.

**Figure 9.** Variability among n=4 random CAR/PDMS 75 µm fibers on mass extracted with retracted fiber (A) and exposed fiber (B), \(t=3\) min, Z=20 mm, \(T=40\) ºC, \(C_{gas}(B)=5.0\) mg m⁻³, \(C_{gas}(T)=5.8\) mg m⁻³, \(C_{gas}(E)=6.2\) mg m⁻³ and \(C_{gas}(X)=5.9\) mg m⁻³.

**Figure 10.** Comparison of the effect of the sample storage time at room temperature on mass loss with retracted fiber (A) and exposed fiber (B); extraction conditions: \(t=3\) min, Z=20 mm, \(T=40\) ºC, \(C_{gas}(B)=5.0\) mg m⁻³, \(C_{gas}(T)=5.8\) mg m⁻³, \(C_{gas}(E)=6.2\) mg m⁻³ and \(C_{gas}(X)=5.9\) mg m⁻³.

**Figure 11.** Relationship between theoretical and experimental mass extracted.

**Figure 12.** SIM chromatograms of TWA sampling of BTEX in exhaust gases with retracted steel needle assembly (without SPME extraction phase) and retracted Carboxen/PDMS 85 µm SPME fiber. Z=5 mm, \(t=60\) min, \(T=25\) to 67 ºC.