Direct Atmospheric Pressure Chemical Ionization-Tandem Mass Spectrometry for the Continuous Real-Time Trace Analysis of Benzene, Toluene, Ethylbenzene, and Xylenes in Ambient Air

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Real-time monitoring of benzene, toluene, ethylbenzene, and xylenes (BTEX) in ambient air is essential for the early warning detection associated with the release of these hazardous chemicals and in estimating the potential exposure risks to humans and the environment. We have developed a tandem mass spectrometry (MS/MS) method for continuous real-time determination of ambient trace levels of BTEX. The technique is based on the sampling of air via an atmospheric pressure inlet directly into the atmospheric pressure chemical ionization (APCI) source. The method is linear over four orders of magnitude, with correlation coefficients greater than 0.996. Low limits of detection in the range 1–2 $\mu g/m^3$ are achieved for BTEX. The reliability of the method was confirmed through the evaluation of quality parameters such as repeatability and reproducibility (relative standard deviation below 8% and 10%, respectively) and accuracy (over 95%). The applicability of this method to real-world samples was evaluated through measurements of BTEX levels in real ambient air samples and results were compared with a reference GC-FID method. This direct APCI-MS/MS method is suitable for real-time analysis of BTEX in ambient air during regulation surveys as well as for the monitoring of industrial processes or emergency situations. (J Am Soc Mass Spectrom 2009, 20, 829–836) © 2009 Published by Elsevier Inc. on behalf of American Society for Mass Spectrometry

Benzene, toluene, ethylbenzene, and isomers of xylene, commonly called BTEX, are volatile organic compounds (VOCs) widely present in petroleum products and added to fuels to increase their octane number [1]. They have toxic health effects depending on duration and levels of exposure [2–5]. In addition, BTEX in urban air contribute significantly to the smog photochemical reactions leading to ozone formation in the troposphere [6].

Several analytical methods have been developed to perform real-time measurements of such compounds in ambient air, and recently, we have published a comprehensive review of the most commonly used on-site methods for continuous real-time monitoring of airborne VOCs [7]. Differential optical absorption spectroscopy (DOAS) has been applied widely for near real-time monitoring of BTEX in ambient air [8, 9], but the presence of oxygen, ozone, and several hydrocarbons with similar spectra gives rise to severe interference effects.

Proton-transfer reaction/mass spectrometry (PTR-MS) has been used in several field studies for real-time monitoring of atmospheric BTEX [10, 11], but there are certain isobaric interferences in the PTR-MS measurements of these hydrocarbons (e.g., notably benzaldehyde).

Other direct-air sampling (DS)-MS methods widely used for real-time determination of BTEX in ambient air are low-pressure chemical ionization/tandem mass spectrometry (LPCI-MS/MS) [12, 13] and atmospheric pressure chemical ionization/tandem mass spectrometry (APCI-MS/MS) [14, 15]. However, they are not yet very conclusive for measuring BTEX in ambient air at low-$\mu g/m^3$ concentrations [7].

The work described in the present article demonstrates the application of a direct APCI-MS/MS system for real-time continuous determination of low-$\mu g/m^3$ levels of atmospheric BTEX. The technique is based on the sampling of air through an atmospheric pressure inlet directly into the APCI corona discharge region. Conventional APCI systems produce protonated-water clusters of the type $(H_2O)_n H^+$ (through a chain of

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ion-molecule reactions starting with N_2^+, O_2^+, NO^+, H_3O^+), those clusters are ultimately responsible for ionizing analytes by proton-transfer [7]. The high collision frequency that occurs at atmospheric pressure between reagent ions and analyte molecules might lead to higher ionization efficiency in APCI compared to LPCI sources. However, one problem associated with APCI is the formation of cluster ions of air and water. These ions make the overall ionization complex and nonquantitative for some compounds, including BTEX-species, particularly at low levels. In addition, at low parts per million concentrations, water inhibits charge-transfer ionization of BTEX-hydrocarbons by solvating reagent ions and thus reduces their ability to interact with hydrophobic molecules [16]. Our approach overcomes these drawbacks by enhancing the efficiency of the chemical ionization of BTEX molecules. The geometry of the direct-air sampling inlet is designed and the sampling flow rate is optimized so that the transfer of charge from primary reagent ions to vapor-phase BTEX occurs with high efficiency.

Experimental

Mass Spectrometry

Experiments were carried out on a TSQ Quantum Ultra AM triple quadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a laser diode thermal desorption LDTD-APCI interface (Phytronix Technologies, Québec, QC, Canada). Details on the LDTD-APCI ion source can be found elsewhere [17]. For our application, the carrier gas line (3 mm i.d.) of the ionization source was used as the air sample introduction line. The system was operated in the positive ion detection mode and without using the laser diode. Because of software built-in safety routines and for a functional gas line system, the LazWell sample plate must be present for the atmospheric pressure inlet of the LDTD-APCI interface to be functional. Optimization of experimental parameters was performed to ensure optimal ionization conditions for BTEX and to maximize ion fragmentation and transmission for each compound. Ion source conditions have been optimized, as well as compound-specific parameters such as collision energy and tube lens offset, which are all important parameters for MS/MS fragmentation experiments and for sensitive detection in the selected reaction monitoring (SRM) mode. The Xcalibur 2.0 software (Thermo Fisher Scientific) was used for optimizing these conditions. The following source parameters were then adjusted to: discharge current 4 μA; capillary temperature 270 °C; sweep gas pressure 0.3 mTorr. Collision gas pressure (Argon) was set to 1.5 mTorr. The peak-width of precursor and product ions was set to 0.7 u at half-height.

Online Gas Chromatography

Comparative experiments were performed by using an online GC-FID BTEX analyzer AirmoBTX1000 (Chromatotec, Saint-Antoine, France) consisting of a sampling unit, a thermodesorber, a 30 m × 0.28 mm i.d. × 1 μm phase thickness MXT30 CE metallic capillary column and a programmable temperature gradient oven. The sampling system comprises one sorption tube filled with selective adsorbent (CarbotrapB). Hydrogen (Hydroxychrom) was used as the carrier gas at a constant flow rate of 3 mL/min. A mixture of zero air (180 mL/min) and hydrogen (26 mL/min) was used for FID supply. The temperature program is as follows: started at 43 °C and ramped to 45 °C at a rate of 2 °C/min and followed by a linear increase of 15 °C/min to 165 °C.

Standard Preparation and Introduction

Analytical grade benzene (Caledon Laboratories, Georgetown, ON, Canada), toluene (Mallinckrodt Specialty, Chesterfield, MO, USA), ethylbenzene (Sigma Aldrich, St. Louis, MO, USA) and xylenes mixture containing 33% of each isomer (Sigma Aldrich) were used as sources of primary standards. Saturated headspace vapors of pure liquid samples were prepared by placing about 2 mL of each compound into different sealed 40-mL volumetric bottles, which were then maintained at 25 °C for over 1 h. Calibration standards were generated by mixing the gaseous headspace samples with ambient air used as diluent gas, to automatically account for any matrix effects. Direct sampling of the ambient air was performed at a flow rate of 3 L/min via an atmospheric pressure inlet through the interface of the LDTD-APCI source using a Teflon-coated pump which is computer controlled by the Phytronix Technologies LazSoft 2.0 software. The saturated headspace samples of BTEX were injected into the ambient air stream using a 500-μL gauge gas-tight syringe (Hamilton Co., Reno, NV, USA) mounted in a syringe pump model 22 (Harvard Apparatus, Holliston, MA, USA). Air flow is then vented outside through a purge pump system. A schematic of the experimental setup is shown in Figure 1. The flow rates of the headspace samples were controlled by the speed of the syringe pump to provide analyte concentrations ranging from 4 to 1300 μg/m^3. The concentrations were calculated based on the known analyte vapor pressure [18] and the chosen dilution factors. Acetone-d6 (Acros Organics, Fair Lawn, NJ, USA) was used as the internal calibration standard (IStd).

BTEX Identification and Quantification

To identify BTEX, Q1 scans were typically performed over a mass-to-charge (m/z) range 30–200. The precursor ions at m/z 78, 92, 106, and 107, corresponding to benzene, toluene, ethylbenzene, and xylenes, respectively, were then selected in the first quadrupole and submitted to collision-induced dissociation (CID) in the second quadrupole. The product ions were filtered by
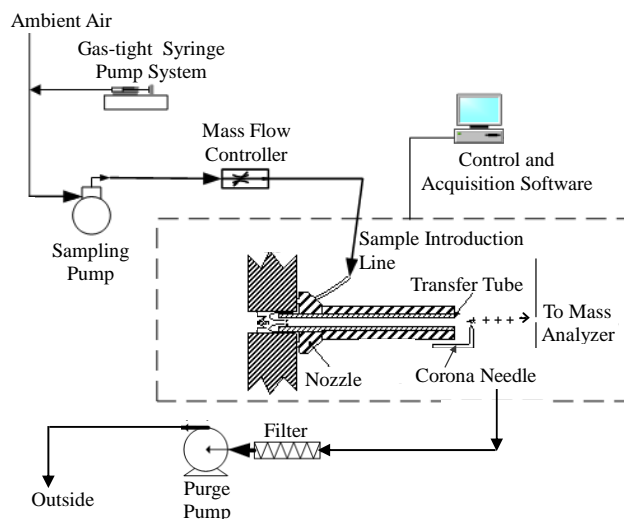
Figure 1. Schematic of the experimental setup.

the third quadrupole and transferred to the detector. Quantification was performed by SRM and by recording the most abundant precursor ion → product ion transition selected for each compound, with a dwell time of 300 ms per transition.

Method Validation

Validation of the direct APCI-MS/MS method was conducted according to the procedure DR-12VMC of the Centre d'Expertise en Analyse Environnementale du Québec (CEAEQ) [19]. This document details the performance characteristics required for the development of analytical chemistry methods. Quality parameters, including linearity, limit of detection (LOD), limit of quantification (LOQ), repeatability, reproducibility, and accuracy, were assessed to validate this method under the optimized conditions.

Multi-point calibration curves (peak average height ratios of analyte over IStd versus the analyte concentration) were constructed for each BTEX. Calibration equations were calculated by using a linear regression method. For each compound, the LOD was determined as three times the standard deviation (SD) of the signal obtained from five replicate injections of the lowest standard concentration, divided by the slope of the calibration curve. LOQs were calculated by using 10-fold SD. The relative standard deviation (RSD) was adopted for repeatability and reproducibility assessment. The repeatability was tested for each compound by analyzing five replicate injections of the lowest standard concentration within 50 min. The reproducibility was estimated by analyzing five replicate injections over five days. The accuracy was evaluated by analyzing a standard mixture of BTEX prepared by spiking a Teflon gas sampling bag (Jensen Inert Products, Coral Springs, FL, USA), filled with zero air (Megs, Ville St-Laurent, QC, Canada), with saturated headspace vapors of pure liquids. The standard mixture was prepared with a known nominal concentration of

each compound and was analyzed as an unknown sample by our method. Accuracy values were expressed as:

$$\text{Accuracy (1\%)} = 100 - \left| \frac{C_{Meas} - C_{Exp}}{C_{Exp}} \times 100 \right| \quad (1)$$

where C_{Meas} is the measured concentration and C_{Exp} represents the expected concentration.

Further evaluation of the performance of our method was carried out by comparison with a reference GC-FID method using real-world samples. Ambient air samples were collected into 56-L Teflon gas sampling bags (Jensen Inert Products) using a Teflon-coated sampling pump at a flow rate of 3 L/min for 15 min. The samples were analyzed by direct APCI-MS/MS and by online GC-FID.

Results and Discussion

Background Mass Spectrum

Although the presence of background ions (i.e., without the addition of any analyte) constitutes the main source of background fluctuations which may impact the method LOD, the number of reagent ions generated in APCI is important because it dictates the amount of target-analyte molecules that can be ionized. The direct-air sampling system of the LDTD-APCI interface is designed and the sampling flow rate is optimized so that the transfer of charge/proton from APCI primary reagent ions to vapor-phase molecules occurs with high efficiency. As a result, although the system was operated under APCI conditions, it exhibited a background mass spectrum that is quite different from that commonly observed with a gas sampling conventional APCI source in ambient atmosphere. As shown in Figure 2, the background mass spectrum (a) of our experimental setup recorded for the ambient air in our laboratory is not dominated by protonated water clusters $(H_2O)_nH^+$ as is commonly seen under usual APCI conditions [20, 21]. The most abundant species in the mass spectrum (a) could be attributed to the ionization of trace amounts of the solvents present in the laboratory air (e.g., protonated acetone at m/z 59). In contrast to the spectrum (a), the background mass spectrum (b) recorded by using the same triple quadrupole instrument brand equipped with an APCI source working at 90 L/min shows a predominant formation of ionized water clusters, the protonated water dimer $(H_2O)_2H^+$ at m/z 37 being the strongest signal. Solvent ions present in the spectrum (a) such as protonated acetone (m/z 59) are very weakly detected in the spectrum (b) in the presence of protonated water clusters. The geometry of the direct-air sampling LDTD-APCI system uses gas dynamics to optimize the sampling efficiency into the assembly formed by the corona discharge region and the MS inlet. The use of low sampling flow rate favors the kinetic of charge/proton transfer from primary reagent ions to gas-phase analyte molecules. The resi-
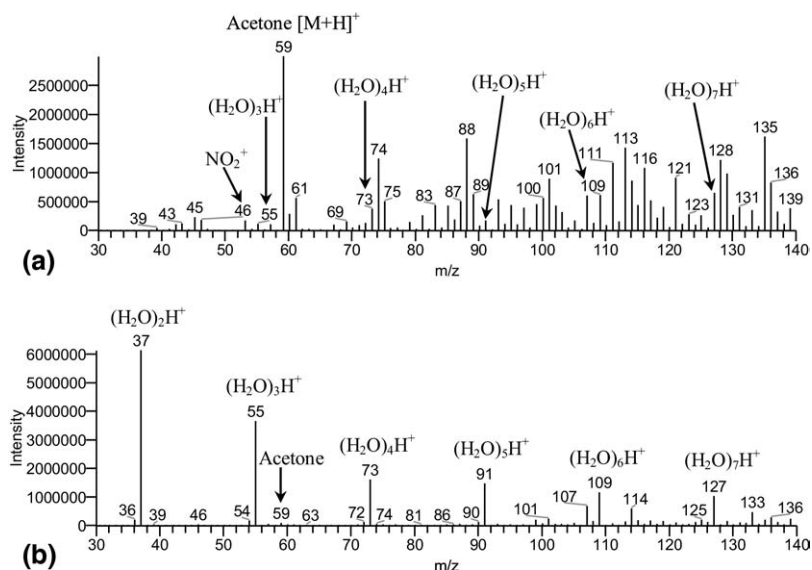
Figure 2. Background mass spectra exhibited by (**a**) the direct-air sampling LDTD-APCI system (3 L/min) versus (**b**) the conventional high-flow (90 L/min) APCI source.

dence time in the source from the corona needle to the MS inlet (around 15 mm long) is governed by the speed of the ions. That speed is the sum of the carrier gas velocity and the ion mobility in the electric field. Assuming that the charged particles are produced in the needle proximity, the average drift speed is about 150 m/s [22], giving a residence time of 10^{-4} s. The carrier gas velocity given by the flow rate of 3 L/min in our case reduces this time by about 4%. Using a high flow inlet at 90 L/min will reduce the transit time by about 60%. On the other hand, the order of magnitude of the collision frequency in the air at room-temperature estimated from gas collision theory [23] is about 10^{11} collisions/s. Maximizing the number of collisions while keeping the properties of gas dynamics provides optimal opportunities for reagent ions in the reaction zone to come into contact with analyte molecules and thereby provides a greater extent of reaction. The resultant completeness of charge/proton-transfer reactions between trace amounts of vapor-phase molecules present in the laboratory air and the primary reagent ions may therefore explain the weak presence of the later in the background mass spectrum (a) of our experimental setup and consequently a greater sensitivity for analyte molecules. This phenomenon was verified by reducing the transit time by moving the needle forward of the MS inlet while keeping all other parameters constant. The water cluster signal increased almost proportionally.

Effect of Air Sampling Flow Rate

The effect of air sampling flow rate was studied to determine the optimal conditions to maximize the sensitivity of the method. This parameter greatly influences the signal intensities of BTEX. In each case, the precur-

sor ion intensity reached a maximum when the air sampling flow rate was 3 L/min and decreased for higher or lower flow rates. These observations suggest that in our experimental conditions, 3 L/min yields the optimal collision frequency leading to the APCI plasma formation and the subsequent charge-transfer to BTEX-species, since the APCI ionization process is initiated through a chain of ion-molecule reactions [7]. Therefore, a constant air sampling flow rate of 3 L/min was used for subsequent experiments.

BTEX-Specific Parameters

The full-scan Q1 mass spectra in Figure 3 show the predominant formation of radical cation $M^{+\bullet}$ at m/z 78 for benzene, m/z 92 for toluene, m/z 106 for ethylbenzene, and protonated ion $[M + H]^+$ at m/z 107 for xylenes. Our observations are consistent with those found in the literature [14, 21, 24]. The ionization process of ambient-air BTEX under APCI conditions was described elsewhere [7]. Benzene, toluene, and ethylbenzene undergo simple charge exchange with reagent ions to produce molecular ions while xylenes, (which have the highest proton affinity among the BTEX family), yield pseudomolecular ions by proton-transfer process with $(H_2O)_nH^+$ ions. The same ionic species are observed in the non-subtract background full-scan mass spectra of BTEX at concentrations determined to be the method LODs (Figure 3). These observations all argue that our approach helps to overcome the inhibition of chemical ionization of low levels of BTEX usually observed for direct APCI [16]. Table 1 summarizes precursor ions, major product ions and SRM parameters optimized for each compound. Identification of the BTEX was done by manual interpretation of the spectra based on their MS/MS fragmentation
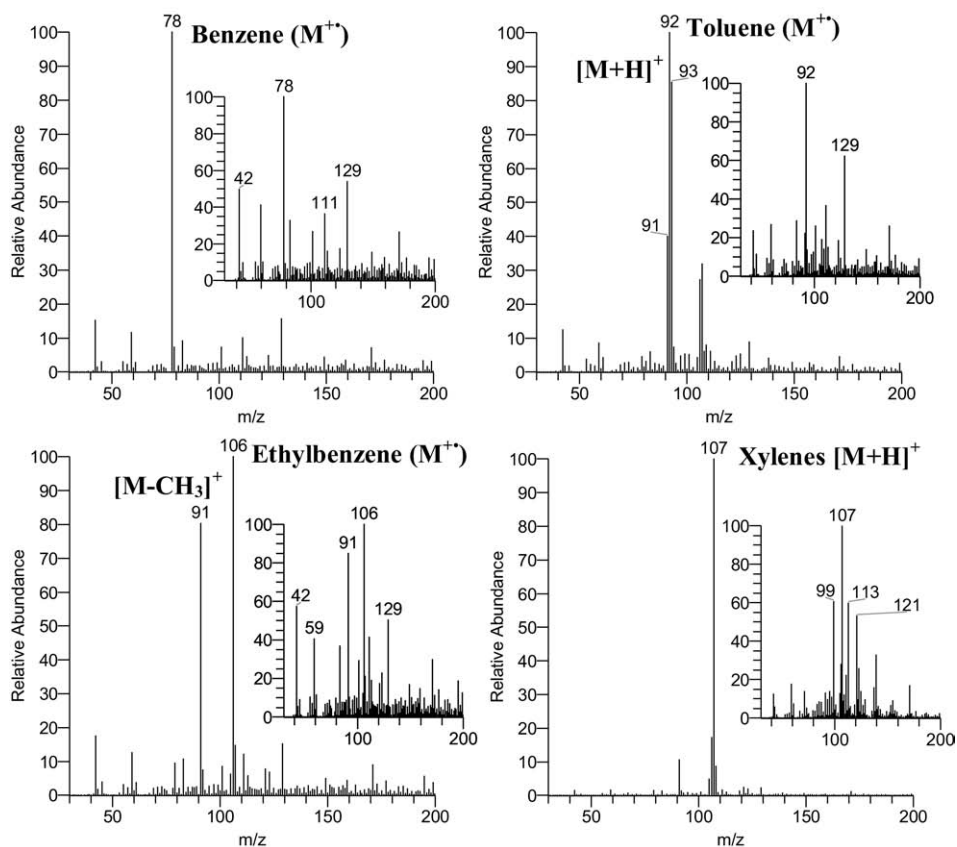
Figure 3. Full-scan Q1 mass spectra of 40 ppb of BTEX recorded in the direct APCI-MS. The insets show mass spectra for lower concentrations (1–2 $\mu g/m^3$).

pattern. Subsequent quantifications were performed using transitions m/z 78 → 52 for benzene, 92 → 65 for toluene, 106 → 91 for ethylbenzene, and 107 → 91 for xylenes.

ble 1). Ambient air without the addition of any BTEX-hydrocarbon was used as the field blank. Peak height stability is achieved within seconds and signal returns to baseline very rapidly when the calibration com-

Linearity

The linearity of the method was evaluated for BTEX in the range from 4 to 1300 $\mu g/m^3$. An example of a BTEX calibration profile using precursor ion → product ion transition is shown in Figure 4. Responses were recorded for five different calibration standards at the optimal experimental conditions described above (Table 1).

Table 1. Optimized parameters for direct APCI-MS/MS determination of BTEX in ambient air

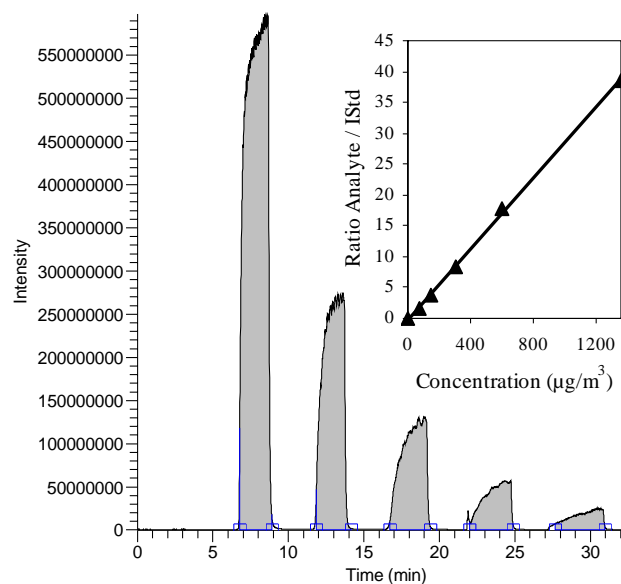|	Precursor ion (m/z)	Collision energy (V)	Tube lens (V)	Product ions
Benzene	78	19	27	52
		29	37	50
Toluene	92	25	40	65
		54	55	39
Ethylbenzene	106	11	39	91
		29	36	65
Xylenes	107	16	46	91
		25	46	65
Acetone-d6	65	23	30	46

Figure 4. Representative calibration profile for BTEX by direct APCI-MS/MS. The inset plot shows a typical calibration curve.

Table 2. Performance parameters of the direct APCI-MS/MS method for BTEX determination in ambient air

	Linear equation (y = ax + b)	LOD (μg/m^3)	LOQ (μg/m^3)	Repeatability (%RSD)*	Reproducibility (%RSD)*	Accuracy		
						Expected (μg/m^3)	Measured* mean $\pm$ SD (μg/m^3)	Percent (%)
Benzene	y = 0.0011x + 0.0418	2	6	7	9	30.8	31.5 $\pm$ 0.9	98
Toluene	y = 0.0025x + 0.0464	1	4	4	7	12.3	11.7 $\pm$ 0.8	95
Ethylbenzene	y = 0.0106x + 0.4850	2	8	8	10	22.6	23.7 $\pm$ 3.9	95
Xylenes	y = 0.0288x − 0.2600	2	5	7	8	31.0	32.2 $\pm$ 2.1	96

*n = 5 replicate analyses.

pound flow is turned off (see Figure 4). This indicates that there is neither a carry-over problem nor ion source saturation problems, validating the performance of the sampling system. After stabilization of the signal, the peak height was used for each calibration level.

Calibration equations for BTEX are presented in Table 2 as $y = ax + b$, where y is the signal height ratio of analyte over IStd, and x is the analyte concentration. The response coefficients (slopes) were significantly different for each compound. This means that the instrument needs to be calibrated for each compound. The calibration curves were linear and covered at least four orders of magnitude, with correlation coefficients of 0.9964 for benzene, 0.9976 for toluene, 0.9965 for ethylbenzene, and 0.9992 for xylenes. At low levels, experiments performed in the range from 4 to 45 μg/m^3 gave good linear correlation coefficients of 0.9970 for benzene, 0.9969 for toluene, 0.9957 for ethylbenzene, and 0.9962 for xylenes. The linear dynamic range (LDR) of the present method is wider than the LDR of 38.3–478 μg/m^3 (for benzene) and 8.6–188 μg/m^3 (for toluene) obtained by Mulligan et al. [14] using a portable cylindrical ion trap mass spectrometer equipped with an APCI source. These results attest to the quantification potential of the method over a wide range of BTEX concentrations from low- and up to high-μg/m^3 levels in ambient air.

Detection and Quantification Limits

LODs for BTEX were in the range 1–2 μg/m^3, whereas LOQs ranged between 4 and 8 μg/m^3 (Table 2). The present method is about 200-fold more sensitive than the current mobile APCI-MS/MS system used by the CEAEQ [25]. This analytical instrument is also a TSQ Quantum triple quadrupole MS, but equipped with a classical high-flow (90 L/min) APCI source, and LODs determined for benzene and toluene by using the same primary standards are 410 μg/m^3 and 190 μg/m^3, respectively. The proposed method is about 10 to 25 times more sensitive than the portable APCI-MS/MS method reported recently by Mulligan et al. [14]. This method is applicable for the monitoring of ambient-air BTEX at trace levels, and our results confirm the quantification potential for ambient concentrations of BTEX in urban air.

Repeatability, Reproducibility, and Accuracy

The repeatability (intra-day precision) and the reproducibility (inter-day precision) expressed as RSD, ranged from 4% to 8% and 7% to 10%, respectively (Table 2). As indicated in Table 2, concentrations of BTEX determined in the spiked standard mixture prepared at known concentrations agreed well with the expected values. Accuracies ranged between 95% and 98%. All these results clearly demonstrated that the values were within the acceptable ranges and the direct APCI-MS/MS method was precise and accurate.

Method Application and Comparison with Online GC-FID

As examples of real-world applications, we present the results obtained for ambient air samples collected from three urban locations in Canada. The first sampling site (#1) is a general mechanics garage where ventilation was controlled by both mechanical and natural systems. The second sampling site (#2) is near the storm drain of an industrial waste landfill site. The third sampling site (#3) is located in a two-lane street in an industrial area. Apart from vehicle emissions and possibly fugitive evaporation, there are no known sources of BTEX in the vicinity of these sites. To further evaluate the performance of our direct APCI-MS/MS method, we performed a comparison with online GC-FID. Following collection in Teflon bags, air samples were transported to the laboratory and analyzed by direct APCI-MS/MS and by online GC-FID. BTEX-species have been successfully detected and quantified in these real air samples by the direct APCI-MS/MS method. Concentrations measured for the BTEX by the two methods are presented in Table 3. BTEX determinations in the real-world air samples by our direct APCI-MS/MS and by the conventional GC-FID method exhibited similar results. We believe that the close agreement of the results obtained by both approaches when analyzing common samples provides strong confirmation for the analytical validity of the method. Although the online GC-FID provides greater sensitivity than DS-MS methods through the preconcentration step, the chromatographic separation and the use of a selective adsor-

Table 3. Mean concentrations ± SD (μg/m^3) of BTEX measured in ambient air samples*

	Site # 1		Site # 2		Site # 3	
	Online GC-FID	Direct APCI-MS/MS	Online GC-FID	Direct APCI-MS/MS	Online GC-FID	Direct APCI-MS/MS
Benzene	9.6	10.0 ± 0.5	1.8	<LOQ	1.2	<LOQ
Toluene	129	123 ± 4	447	419 ± 17	48	43 ± 2
Ethylbenzene	9	10 ± 1	10	13 ± 1	2	<LOQ
Xylenes	46	49 ± 6	49	55 ± 4	9	10 ± 1

*n = 5 replicate analyses for direct APCI-MS/MS measurements of BTEX in each sample.

bent that discriminates against other components in air, the latter are generally considered more reliable for the measurement of BTEX in the ambient air because of their real-time continuous monitoring capabilities [7]. The APCI-MS/MS analysis was accomplished with a fast response time (less than 10 s) instead of the 20 min required by the GC-FID method.

Conclusions

Unlike other methods (such as DOAS and PTR-MS), the method developed in this study is free of interference effects from oxygen, ozone, or isobaric hydrocarbons. The presence of small peaks of protonated ethylbenzene at m/z 107 and xylene molecular ion at m/z 106 in the mass spectra of BTEX (Figure 3) did not give rise to interference effects when analyzing air samples containing both compounds. The accuracy values (over 95%), and the close agreement of the results obtained by our method and the online GC-FID when analyzing common samples clearly demonstrated that these potential interferences do not have significant effects. Competition processes may take place when both hydrocarbons are present in the same mixture and the ethylbenzene may undergo charge-transfer ionization exclusively, whereas xylenes undergo proton transfer reaction. Therefore, ethylbenzene and xylenes can be distinguished and measured individually by the present method. However, as observed for the GC methods, which are often unable to separate m- and p-xylenes, this method cannot provide isomer-specific data for o-, m-, and p-xylenes. The analytical characteristics of the present direct APCI-MS/MS method make it suitable for real-time continuous monitoring of atmospheric BTEX at near background levels as well as up to high concentrations found in industrial or emergency-type situations. The current application is based on Teflon gas sampling bags but the project will later focus on the validation of the method by using a mobile triple quadrupole instrument (e.g., an instrument installed in a motorized vehicle [7, 25]). Moreover, we plan to use reactant gases to improve this method to render it more sensitive for determination of BTEX at lower and lower levels.

Acknowledgments

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