

Air sampling of aromatic hydrocarbons in the presence of ozone by solid-phase microextraction

Gouhua Xiong, Jacek A. Koziel*, Janusz Pawliszyn¹

Department of Chemistry, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

Abstract

Effects of ozone on air sampling of standard gas mixtures of aromatic hydrocarbons were tested using solid-phase microextraction (SPME). Standard concentrations of ozone ranging from 10 ppb (v/v) to 6400 ppm (v/v) were generated using an in-house built ozone generator based on corona discharge. Effects of temperature, discharge voltage, and oxygen flow on the ozone generation were tested. The working dc voltage had the greatest effect on generated ozone concentration and was proportional to the ozone concentration. Generation temperature and oxygen flow rate were inversely proportional to ozone concentrations. Produced ozone was mixed with standard benzene, toluene, ethylbenzene, and xylenes (BTEX) gas at less than 100 ppb (v/v). Air samples were collected with poly(dimethylsiloxane) (PDMS) 100 μ m SPME fibers and analyzed by gas chromatography (GC)–flame ionization detection (FID) and GC–MS. Significant reductions of BTEX concentrations were observed. In addition, some products of BTEX–ozone–oxygen reactions were identified. SPME worked well as a rapid sampler for BTEX and BTEX–ozone–oxygen reaction products. No significant deterioration of the PDMS coating and no significant reduction of absorption capacity were observed after repeated exposure to ozone.

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1. Introduction

Ozone is a common and primary air pollutant that is extremely important in ambient and indoor air chemistry [1,2]. Solid-phase microextraction (SPME) combines sampling, pre-concentration and the direct transfer of the analytes into a standard gas chromatography (GC) system [3]. To date, SPME has been successfully applied in numerous environmental, food, flavor, pheromone, pharmaceutical, clinical and forensic applications [4–6]. Several research studies have focused on the application of SPME to air sampling and human breath analysis [7–10]. SPME sampling methods have been developed for total volatile organic compounds (TVOCs), formaldehyde and volatile organic sulfur compounds in the air [11–15]. SPME can also be interfaced with conventional autosamplers for continuous VOC sampling and analysis of a moving air stream [16]. SPME may

also be used for time-weighted average (TWA) sampling [17–19]. SPME has been applied to indoor air surveys of benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds with fast, portable GC [20,21]. Recently, a novel methodology for rapid air sampling of BTEX with solid SPME fibers was developed and tested [22–24]. It is feasible to use SPME for ambient air sampling. It is also convenient to use SPME for qualitative characterization of reaction products and for screening of air and air samples. In this research, we attempted to evaluate the effects of ozone on SPME sampling of BTEX in air.

2. Experimental

2.1. Ozone generator

Ozone was generated in a specially designed and built generator (Fig. 1). The generator consisted of a flow trough glass bulb with a corona discharge. The generator consisted of 3 long bulbs (outside, middle, and inside) nested in each other. Pure oxygen (UHP grade from Praxair, Waterloo, Canada) was first fed between the outside and the middle bulbs and then routed between the middle and the inside

* Corresponding author. Present address: Texas A&M University, Texas Agricultural Experiment Station, 6500 Amarillo Boulevard, Amarillo, TX 79106, USA. Tel.: +1-806-677-5619; fax: +1-806-677-5644.

E-mail addresses: koziel@tamu.edu (J.A. Koziel), janusz@uwaterloo.ca (J. Pawliszyn).

¹ Tel.: +1-519-888-4641; fax: +1-519-746-0435.

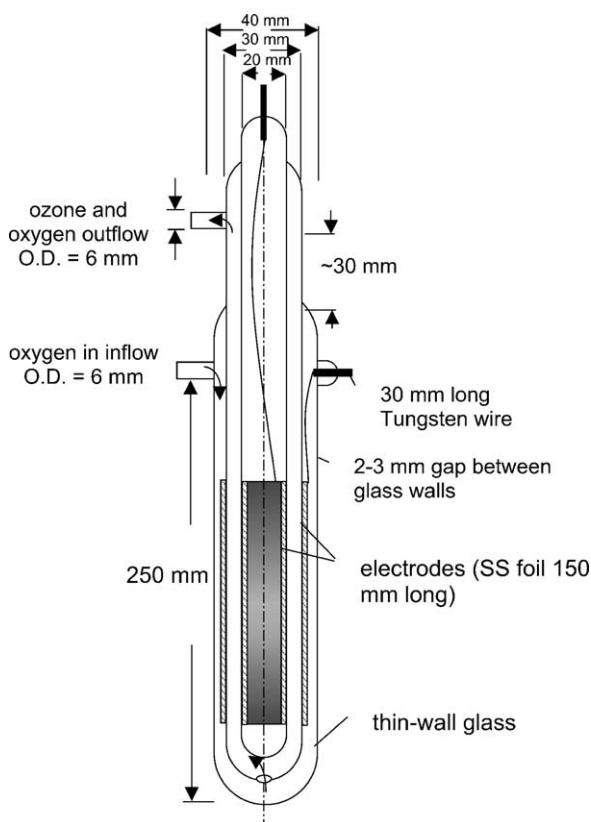


Fig. 1. Schematic of ozone generator.

bulb. The oxygen passed between the two stainless steel foil electrodes, the outside electrode wrapped around the middle bulb and the electrode inserted in the inside bulb. The distance between the electrodes was approximately 5 mm. A high dc voltage was connected to the tungsten leads causing corona discharge. The voltage output was regulated by a Variac controller. The ozone generator bulb was placed inside a Styrofoam cooler filled with dry ice. The whole setup was placed in a rugged wooden box for glass bulb protection and insulation, and worker's safety. The temperature was regulated by the amount of dry ice around the glass bulb. The temperature of the glass bulb was monitored with a thermocouple and HH-20 thermometer (from Omega). The combination of low temperature, corona discharge, and the oxygen flow resulted in the conversion of a fraction of oxygen into the ozone.

2.2. Ozone measurements

Ozone concentrations downstream from the generator were measured using a hand pump and colorimetric tubes. The pump (Accuro Pump, from Dräger) pulled a 100 ml air sample through the tube with each stroke. The one-handed operation of the pump is simple because a built-in stroke counter indicates exactly how many strokes and therefore what air volume has been taken. The visual end-of-stroke indicator confirms the completion of each pump stroke. The

disposable sampling tube produced a color change in the presence of ozone. The length of color change and color intensity indicates the amount of ozone pumped through the tube and can be related to concentration. Method detection limits were approximately 5 ppbv (v/v) with 100 strokes per sampling. Sampling times are typically a few minutes per 100 strokes.

2.3. Standard gas generation of BTEX

Traceable to the US National Institute of Standards and Technology (NIST) standards and certified permeation tubes (from Kin-Tech) were used for the generation of benzene, toluene, ethylbenzene, and *o*- and *p*-xylene (BTEX). Ultra-high purity air at 50 psi was used to dilute BTEX vapors generated in the flow-through glass bulb that was kept at constant temperature of 50 °C (1 psi = 6894.76 Pa). The air flow through the glass bulb (oven flow) and the by-pass dilution air was controlled with two mass flow controlled (from Sierra Instruments), 500 and 5000 ml/min, respectively. The bulb was inserted in a heated aluminum enclosure that served as a heat sink and was heated with two 100 W heating rod elements and feedback thermocouple. The temperature in the glass bulb was maintained within 0.1 °C using an electronic heat control device designed and constructed by the Electronic Science Shop (University of Waterloo, Canada).

Concentrations of BTEX were determined as the ratio of permeation rates for each tube and the air flow rate. The permeation (emission) rates for each tube were estimated as a ratio of mass loss (determined by biweekly weighing of permeation tubes) and elapsed time. The standard gas concentrations were 64, 21, 4.1, and 4.8 ppbv for benzene, toluene, ethylbenzene, and *p*-xylene respectively. The relative standard deviations for concentrations ranged from 1.6% for benzene to 4.8% for *p*-xylene as determined by sampling with SPME.

Standard BTEX gas was generated and directed into the flow-through sampling bulb equipped with half-hole septa (from Supelco) for the insertion of SPME fibers into the gas stream. The temperature of the sampling bulb was maintained at room temperature. Standard ozone and air mixture were delivered through the T-connection between the standard gas generator and the sampling bulb (Fig. 2).

2.4. SPME sampling and sample analyses

Gas samples of BTEX and products of BTEX reactions with ozone were collected using the poly(dimethylsiloxane) (PDMS) 100 μm SPME (from Supelco) coating. Sampling time for all SPME samples was 5 min. Each sample was analyzed immediately by GC-flame ionization detection (FID) (model 8610 from SRI Instruments). A Pona capillary GC column (50 m × 0.2 mm, 0.5 μm film thickness Hewlett-Packard, Mississauga, Canada) was used. The GC oven temperature was linearly programmed from 30 to 250 °C at a ramp of 15 °C/min. The high purity air for FID

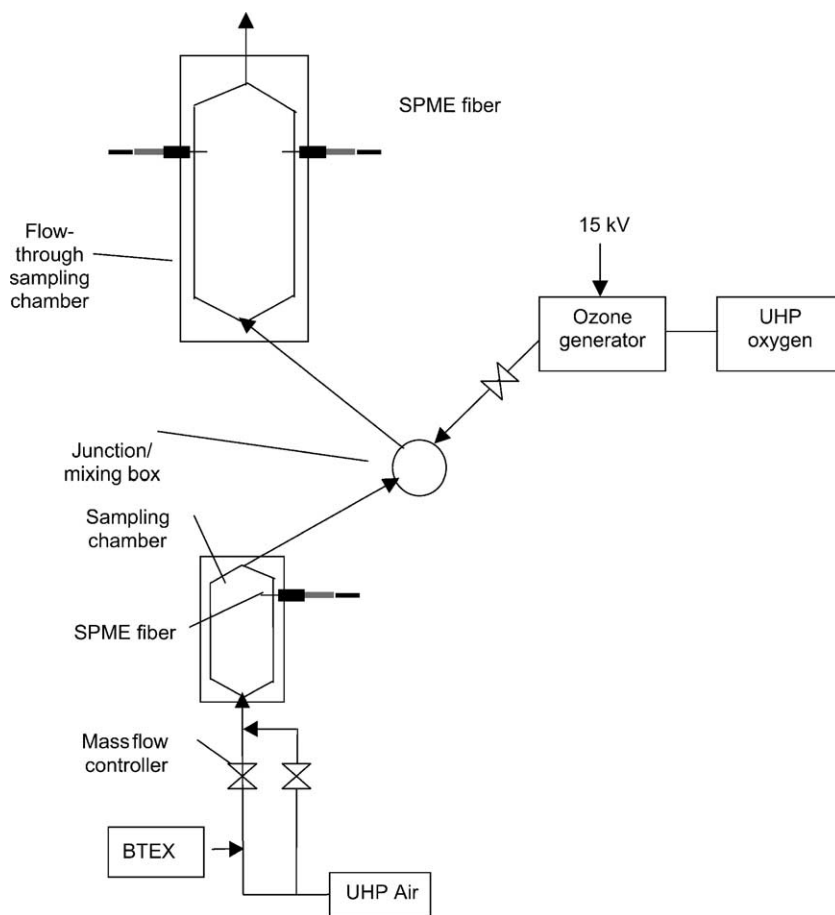


Fig. 2. Schematic of gas sampling setup.

was supplied from a built-in air pump in the SRI GC system. Ultrahigh purity (UHP) hydrogen gas was used both as the GC carrier gas, with a flow rate of 4.0 ml/min, and the FID combustion gas.

Preliminary identification of some products of ozone and BTEX reactions was carried out on a 6890 series GC system equipped with a 5973 mass-selective detector (Agilent, USA) fitted with a 30 m × 0.25 mm, 0.25 μm HP-MS5 column. The carrier gas was UHP helium (Praxair) at 10 psi (constant pressure mode). The injector temperature was 210 °C and the column oven temperature was ramped from 50 to 100 °C at 5 °C/min, 100 to 160 °C at 10 °C/min, holding for 2 min, and 160 to 280 °C at 20 °C/min. The conditions for the MS system were set as follows: total ion current mode, EM voltage at 1600 V, the transfer line temperature at 280 °C, quadruple temperature at 150 °C, and MS source temperature at 230 °C.

3. Results

3.1. Ozone concentrations

The generation of ozone was simultaneously controlled by three main parameters namely working dc potential, ozone

generator temperature, and the oxygen flow rate. The ozone concentrations obtained with the ozone generator by varying the mentioned three parameters ranged from 10 ppbv to 6400 ppmv (v/v). For example, an ozone gas with a concentration of 10 ppbv was obtained when conditions were controlled as follows: O₂ flow rate = 150 ml/min, working dc potential = 5000 V, and the foam insulation box around the ozone generator was fully filled with dry ice (the temperature = −80 °C). The lowest ozone concentration (10 ppbv) was similar to typical ambient ozone concentrations in ambient air. The maximum ozone concentration of 6400 ppmv was much higher than some elevated ozone concentrations in urban air reaching 500 ppbv [1].

3.2. Effects of voltage, generation temperature, and oxygen flow on ozone generation

The maximum working potential provided by a dc transformer could reach as high as 11,400 V. The minimum working potential that the ozone generator requires is 4000 V, but the Variac did not work well when the potential was lower than 5000 V. Table 1 summarizes ozone concentrations obtained by varying the dc voltage from 6000 to 11,000 V. The resulting ozone concentration was proportional to applied

Table 1
Effect of working dc potential on ozone generation

Working potential (V, dc)	Ozone concentration (ppmv)
6000	3
7000	180
8000	1000
9000	3500
10000	5000
11000	6400

Note: O₂ flow rate was 60 ml/min and the foam box was filled with dry ice up to 1/3 height (the temperature of the gas phase inside the box was about -35°C).

dc voltage and varied from 3 to 6400 ppmv for 60 ml/min oxygen flow and the generation temperature of -35°C .

Table 2 summarizes the resulting ozone concentrations as functions of oxygen flow rate and the generation temperature. The results indicate that the ozone generation is inversely proportional to the oxygen flow rate and inversely proportional to the generation temperature. The oxygen flow rate was set at 60, 150, and 250 ml/min and the generation temperatures were -35 , -65 , and -80°C . These temperatures corresponded to the level of dry ice in the insulating

box around the glass bulb from 1/3 full (treatment “A”), 1/2 full (treatment “B”), and full (treatment “C”), respectively. The dc voltage was maintained at 11,000 V. The ozone concentration data summarized in Tables 1 and 2 suggests that the most important parameter in controlling the ozone generation is the working dc potential. The effects of generation temperature and the oxygen flow are significant, but not as great as those caused by the dc voltage.

3.3. Reactions between BTEX and ozone

Ozone and BTEX were simultaneously introduced into a sampling chamber (Fig. 2). They were well mixed at the entrance end of the chamber and then go through the chamber. The hydraulic residence time in the sampling chamber was approximately 10 min. The BTEX gas samples and the products of BTEX–ozone reactions were collected with the SPME fibers and analyzed immediately by GC–FID and GC–MS. It was observed that there were no significant reduction of BTEX concentrations and therefore no reactions between ozone and BTEX when the concentration of ozone was lower than 800 ppmv (before mixing with BTEX). Numerous new compounds

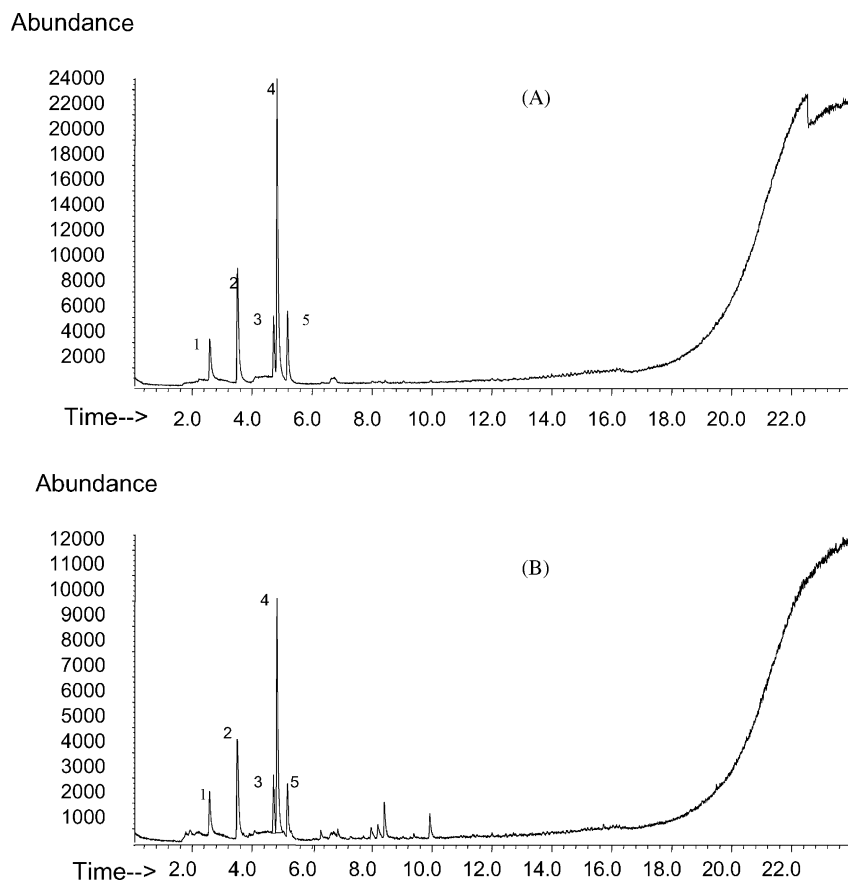


Fig. 3. GC–MS chromatograms of BTEX alone and the mixture of BTEX and the products of BTEX–ozone reactions. (A) BTEX alone; (B) mixture of BTEX and the products of BTEX–ozone reactions (O₂–O₃ flow: 150 ml/min; O₃ concentration before mixing with BTEX: 2400 ppmv). BTEX were diluted by O₂–O₃ introduced besides the reactions. SPME was carried out for 5 min using a PDMS 100 μm coating for both of samples. Compounds indicated: (1) benzene; (2) toluene; (3) ethylbenzene; (4) *p*-xylene; (5) *o*-xylene. Time scales in min.

Table 2
Effects of generation temperature and oxygen flow rate on ozone generation

	O ₂ flow rate 60 ml/min			O ₂ flow rate 150 ml/min			O ₂ flow rate 250 ml/min		
	A	B	C	A	B	C	A	B	C
Ozone concentration (ppmv)	6400	5100	4700	2400	1600	1300	1400	1100	1000

Note: Working dc potential was 11,000 V. (A) The foam box was filled with dry ice up to 1/3 height; (B) to 1/2 height; and (C) fully filled. The temperatures of the ozone generator were -35 , -65 and -80 °C for A, B and C, respectively.

Table 3
Reduction of BTEX concentrations (%) in the presence of ozone

Compounds	O ₂ flow rate 60 ml/min			O ₂ flow rate 150 ml/min			O ₂ flow rate 250 ml/min		
	A	B	C	A	B	C	A	B	C
Benzene	-8.6	-8.1	-6.3	-12.2	-10.8	-8.8	-1.4	-5.9	-2.8
Toluene	-21.3	-19.5	-17.1	-19.8	-14.2	-12.5	-11.8	-6.1	-5.0
Ethylbenzene	-23.5	-19.5	-18.3	-24.0	-19.8	-12.1	-9.6	0.0	-4.4
<i>p</i> -Xylene	-43.1	-40.2	-35.6	-34.6	-30.4	-22.7	-21.9	-13.9	-13.1
<i>o</i> -Xylene	-41.4	-39.6	-32.7	-32.0	-25.1	-24.3	-15.3	-8.2	-6.9

Note: Working dc potential for the ozone generator was at 11,000 V (dc). (A) The foam box was filled with dry ice up to 1/3 height; (B) to 1/2 height; and (C) fully filled. The temperatures of the gas phase inside the box were about -35 , -65 and -80 °C for A, B and C, respectively.

were produced by reactions between the BTEX, oxygen and ozone (Fig. 3). The new compounds that were tentatively identified using built-in NIST spectral library included 2-ethyl-1,3-hexanediol, propoxyphene, benzaldehyde, acetophenone, 4(3)-methyl-benzaldehyde, nonanal, and decanal. No peak of ozone was detected, indicating that the PDMS 100 μ m coating is not efficient in extracting ozone.

Table 3 summarizes reductions in BTEX concentrations in the presence of ozone. The ozone concentrations measured were identical to those listed in Table 2. Experimental results indicate that the rates of reactions were different for each BTEX compound with exception of xylene isomers. Similarly, the rates of reaction for toluene and ethylbenzene were also close to each other. The greatest reduction of concentrations were observed for xylene isomers, followed by ethylbenzene and toluene, and benzene, respectively, for all treatments tested. The results indicate that SPME can serve as a convenient sampler for monitoring of reactions between BTEX and ozone. Such reactions are common in ambient urban air and play an important role in the photochemical interactions.

3.4. Long-term effects of ozone on PDMS 100 μ m coating

Extraction characteristics for SPME were not affected by ozone when the ozone concentrations were less than 800 ppmv, i.e., when no reactions between BTEX and ozone were observed. No significant change of absorption capacity was found after frequent use of the same PDMS 100 μ m coating during a 4-month period during which SPME fiber was exposed to BTEX standard gas, O₃-O₂ gas mixtures, and pure oxygen.

4. Conclusions

Standard gas concentrations of ozone were generated using oxygen and corona discharge in the generator that was built and tested. Several operating parameters including dc voltage, generation temperature and oxygen flow rate were tested. The generated ozone was mixed with BTEX standard gas and the BTEX reduction and reaction products were sampled with SPME and characterized with GC-FID and GC-MS. Several conclusions stem from research:

- (1) Stable ozone concentrations can be produced in the laboratory using a flow-through system with oxygen supply, high dc voltage, and low temperature. Generated ozone concentrations were as low as 10 ppbv to as high as 6400 ppmv. Generated ozone could be easily mixed with other standard gases in a flow-through sampling system.
- (2) The dc voltage is the most important parameter affecting ozone concentrations. The generated ozone concentrations are proportional to the dc voltage used. The effects of oxygen flow rate and generation temperature are inversely proportional to the resulting ozone concentration, but their effects are not as great as those of dc voltage.
- (3) SPME can be used as a convenient sampler for rapid extraction, quantification, and characterization of reaction products. Many of these compounds are important components of urban air atmospheres. SPME could also serve to evaluate the reduction of selected VOCs by commercial air cleaners based on ozone generation.

- (4) The absorption capacity of the PDMS 100 μm SPME coating was not affected by the repeated exposure to ozone and oxygen. No significant deterioration of the PDMS coating was observed during this study.

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