

System for the generation of standard gas mixtures of volatile and semi-volatile organic compounds for calibrations of solid-phase microextraction and other sampling devices

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Abstract

Standard gases are used for quality control and quality assurance, development of analysis methods and novel air sampling devices. The use of solid-phase microextraction (SPME) and other novel technologies for research in the area of air sampling and analysis requires systems/devices for reliable standard gas generation and sampling. In this paper we describe a new gas standard generating system for volatile organic compounds (VOCs) and semi-VOCs that was designed, built, and tested to facilitate fundamental and applications research with SPME. The system provided for the generation of a wide range of VOC/semi-VOC concentrations and mixing various standard gases, estimation of detection limits, testing the effects of sampling time, air temperature and relative humidity, testing the effects of air velocity and ozone on sampling/extractions. The system can be also used for calibrations of analytical instrumentation, quality control and quality assurance checks, and cross-validations of SPME with/and other sampling techniques.

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1. Introduction

Volatile organic compounds (VOCs) are considered one of the major components of indoor and outdoor air pollution. Development of sampling and analysis methods for VOCs in air requires the use of reliable gas standards, and particularly ones that appropriately simulate the environment of interest. There are many methods for gas standard generation of VOCs in the laboratory that are alternative to the use of specialty certified and compressed gases. Simple methods to generate standard gases in enclosed, batch-type containers include the injection of liquid and evaporation into a defined air volume and liquid standard-headspace equilibrium-based methods. Continuous gas generation and

flow through systems have advantages over batch-type systems such as (1) minimization of the effects of adsorption to (wet) surfaces of the system, (2) continuous range dilution, (3) ease of flow and analyte mixing, (4) ease of air sample conditioning for temperature, relative humidity, and control of air velocity, and (5) the generation of practically an unlimited supply of standard for analytical purposes. The latter is particularly important in cases where sampling volume could affect sampling (extraction). This is the case with air sampling via solid-phase microextraction (SPME) [1], where VOCs extractions can be affected by volume limitations [2].

There are several conventional methods for continuous generation of VOCs gas standard including: (1) continuous syringe pump injection, (2) diffusion methods, (3) evaporation methods, (4) electrolytic methods, (5) chemical methods, and (6) permeation methods [3]. Syringe injectors or pumps for injections of liquid standard into an air stream are extensively used since 1950s for generation of standard gases in many applications, e.g., in inhalation toxicity studies [4], validation of direct-reading air quality samplers [5], and generation of air pollution standards [6]. Syringe pumps are available with discrete or variable speeds. The delivery rates for different models range from approximately 1 μl to

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140 ml/min [3]. The disadvantages are associated with the limitations to syringe volume and the need to periodic refill. Also, significant fluctuations of delivery rate inherent to some syringe pumps may require large retaining/mixing chambers to minimize concentration fluctuations. Diffusion methods rely on uniform rate of diffusion through tubes if the temperature, concentration gradients, and tube geometry remain constant. These methods provide a simple means of obtaining vapor concentrations between 0.1 and 100 ppm (v/v) (ppmv) for VOCs [3,7]; however, the temperature has to be controlled within $\pm 0.2^\circ\text{C}$ to maintain $\pm 1\%$ accuracy [3,8]. Evaporation methods use diluent gas bubbled through or passed over a liquid [9]. Such methods work well for single analytes; however, they are not suitable for mixtures. Electrolytic methods can generate gases such as NO, NO₂, CO₂ that are released from side reactions occurring during electrodeposition of metal ions from solution [10]. This is a very fast method of generating gases; however, it is critical to control the process by assuring sufficient amount of electrolyte and diversion of gases produced at the other electrode [3]. Other unwanted effects of electrode heating and lower yields than theoretically predicted need to be considered. Chemical methods use gas–liquid or gas–solid reactions to generate standard gas. These methods are feasible when the gas is very reactive and generally not available or extremely expensive [3,11]. Permeation methods are considered one of the best and have been used since the 1960s [3,12,13]. These methods use a sealed polymeric container filled with an analyte, which in turn dissolves and permeate through the walls of container at a constant rate for a given temperature. Permeation works extremely well for analytes capable of maintaining gas–liquid equilibrium inside a container (typically tube). All conventional methods are summarized elsewhere [3]. Novel methods based on thermal decomposition of bonded compounds to silica gel or glass surfaces [14–16] and microwave-assisted generation [17] have been introduced.

In the recent decade, SPME was introduced and then applied to air sampling and analysis [1,18]. SPME sampling methods have been developed for total volatile organic compounds (TVOCs), formaldehyde and volatile organic sulfur compounds in air [19–21]. SPME can also be interfaced with conventional autosamplers for continuous VOC sampling and analysis of a moving air stream, human and bovine breath [22–24]. Two studies indicated that SPME may also be used for time-weighted average (TWA) sampling [25,26]. SPME has been applied to indoor air surveys with fast, portable gas chromatography (GC) [27,28]. A novel methodology for rapid air sampling with solid SPME fibers was developed and tested [29,30].

Because of the growing number of SPME applications and other novel technologies for air sampling, methods development, and the amount of fundamental research to be completed, there is a need for a gas standard generation system that could be interfaced with sampling chambers for a wide range of sampling/extractions from air. Sev-

eral researchers reported the use of standard gases with SPME. Gorlo et al. [31] used permeation through PTFE membrane-based devices for generation of carbon tetrachloride, toluene, chlorobenzene, *p*-xylene, and *n*-decane, and calibrations with SPME [31]. Martos and Pawliszyn demonstrated the use of the standard gas generation system toward the accurate understanding of the physical chemical properties of the SPME coating [19]. This work demonstrated the concepts in grab sampling with SPME and also presented the first use of SPME as a time weighted average sampler in industrial air. The standard gases were generated using a syringe pump delivery system and a flow through 20l chamber to attenuate any fluctuations in vapor concentrations. The system was further used by Martos and Saraullo for the generation of more than 100 different airborne paraffins, isoparaffins, aromatics, naphthenes and olefins and their analyses with SPME, which enabled the researchers to demonstrate the relationship between chromatographic retention index and analyte mass loading [32]. This work led to the development of sampling air with SPME for determination of TVOC, a parameter often used as a marker of indoor air quality. Martos and Pawliszyn also used permeation tubes filled with paraformaldehyde and a commercial standard gas generator to prepare formaldehyde standards for on-fiber derivatization with SPME [20]. This work demonstrated the application for grab sampling air of formaldehyde (10s) and the use of SPME as a time weighted average sampling device (8h) specific for formaldehyde. Spinhirne and Koziel also used permeation tubes to prepare standard gas mixtures of volatile fatty acids and used SPME for quality assurance and quality control [33]. Koziel and coworkers used permeation tubes and a syringe pump to generate gas standards for benzene, toluene, ethylbenzene, xylenes (BTEX), and *n*-alkanes [34]. Jia et al., used the same system to generate gas standards for BTEX [27]. Koziel and coworkers used standard BTEX gases from this system to develop and further test the rapid air sampling methodologies with SPME [29,30]. Koziel et al. used formaldehyde standards for calibrations in the field air sampling [35]. Martos and Pawliszyn used the standard gas generation systems to thoroughly describe SPME as a time weighted average sampler [25] and Khaled and Pawliszyn generated *n*-alkanes to further explore the concept of TWA sampling using SPME [26]. These studies required the delivery of a constant and reliable source of standard gas over long periods of time, which was readily accomplished with the standard gas generation systems described herein.

In this paper, we describe a standard gas system that was built and tested at the New Analytical Methods and Technologies Laboratory at the University of Waterloo. Several research studies were completed using parts of this system. We describe the standard gas generating system and present selected validation data that compares SPME as an air sampling tool and recognized air sampling approaches, namely NIOSH methods for air sampling and analysis.

2. Experimental

2.1. Standard gases system

The system consisted of three separate and continuous standard gas generators and air sampling chambers capable of providing wide ranges of concentrations for VOCs and semi-VOCs in the air. These included benzene, toluene, ethylbenzene, *p*-xylene, chlorinated VOCs, formaldehyde and *n*-alkanes which were generated at controlled air temperatures and relative humidities. Standard gas generation for BTEX, chlorinated VOCs, and formaldehyde was achieved using permeation tubes. For all *n*-alkanes, that is C₅H₁₂ to C₁₅H₃₂, a direct injection of the analytes into an air stream was used. Additional components of this system are an ozone generator [36], graduated flow-through chamber [29], and a mixing flow-through chamber with heating and cooling. Heating was achieved with a heating tape and heat control device. The cooling was achieved with a 10 mm i.d. plastic tubing wrapped around the bulb (Fig. 1) which was supplied with chilled (laboratory) water. As a result, the range of temperatures for standard gases was from 5 to 40 °C. The additional components could be connected in several combinations, which allowed for great flexibility of experimental

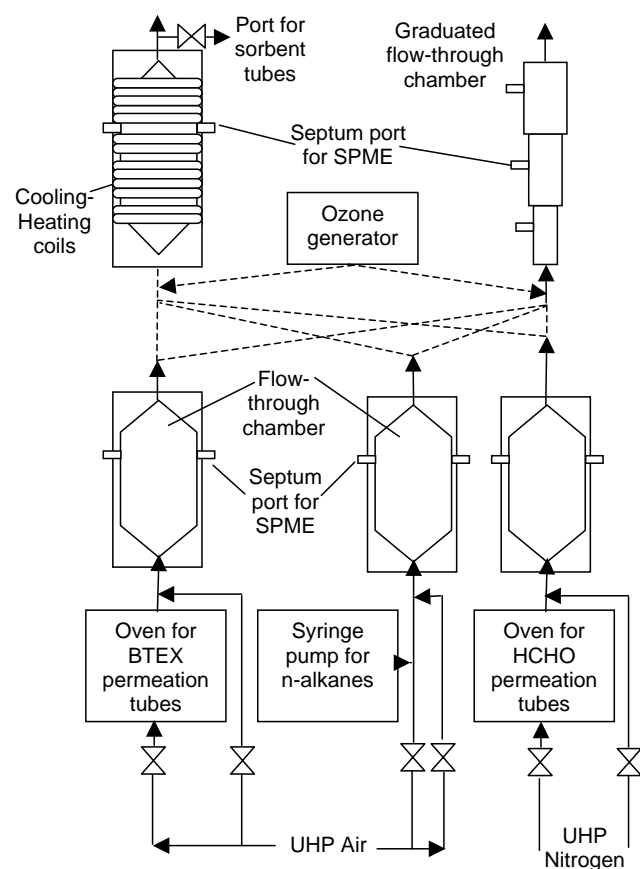


Fig. 1. Schematic of standard gas generating system for research with SPME.

designs. A general schematic of the standard gas system is provided in Fig. 1.

2.2. Permeation tubes

US National Institute of Standards and Technology (NIST) traceable certified permeation tubes (Kin-Tek, La Marque, TX, USA) were used for benzene, toluene, ethylbenzene, *p*-xylene (BTEX) and formaldehyde generation [34]. A Kin-Tek standard gas generator (Kin-Tek) (model 491MB) was used to generate standard gas concentrations of formaldehyde. Ultrahigh purity nitrogen (for Kin-Tek standard gas generator) and air (for VOCs and *n*-alkanes generators) at 3.4 atm (50 psi, 1 psi = 6894.76 Pa) were supplied using thoroughly cleaned 3 mm i.d. (1/8 in.) copper tubing and Swagelok connectors. Supplied air was additionally scrubbed using Supelpure-HC hydrocarbon trap (Supelco, Mississauga, Canada) prior to entering the standard gas generating devices. Permeation tubes for chloroform, 1,1,1-trichloroethane (1,1,1-TCA), and trichloroethene (TCE) were made by placing pure analyte inside 100 mm long (1/4 in.) PTFE tubing capped with 20 mm long solid PTFE plugs and 6 mm (1/4 in.) Swagelok caps. Chloroform was purchased from Sigma–Aldrich (Mississauga, Canada). TCE and 1,1,1-TCA were purchased from Caledon (Georgetown, Canada). Emission rates for each permeation tube were verified by periodic monitoring of weight loss of individual analytes using an Ohaus Analytical Plus scale [34].

2.3. Permeation oven

All permeation tubes were placed inside a glass cylinder (Kin-Tek) and swept with constant flow of dilution air. The permeation cylinder was held inside a permeation oven (100 mm outside diameter, 45 mm inside diameter, 200 mm high) machined from a solid aluminum rod. Two 100 W heating rods were placed inside small holes approximately halfway between the inside and outside diameters of the aluminum cylinder. The temperature of the permeation cylinder was controlled by a K-type thermocouple (Omega, Stamford, CT, USA) and an electronic heat control device designed and constructed by the Electronic Science Shop (University of Waterloo, Canada) [34].

2.4. Syringe pump injection

For *n*-alkane standard gas generation, a Razel Scientific Instruments syringe pump (model A-99) and 500 µl Gastight Hamilton syringe were used to deliver the *n*-alkane mixture through a Thermogreen LB-2 septum into a heated Swagelok mixing tee. The mixing tee on the primary air line to the chamber was heated to 90 °C using a heating tape controlled with a variable voltage controller. The preparation of mixture was completed by spiking appropriate amounts of *n*-alkanes using a 10 µl Gastight Hamilton syringe through a PTFE-lined septum, starting with the least volatile, to a

pre-weighed 15 ml vial. After spiking each compound, the vial was re-weighed. After preparation, the vial with the standard mixture was manually agitated, and equal aliquots were dispensed into 2 ml vials (with no headspace left) equipped with PTFE-lined septa.

Standard *n*-alkane mixture was then transferred from vials into a 1 ml Gastight Hamilton syringe and placed in the syringe pump. The mixture delivery rate was confirmed through three independent approaches. In the first approach, the pre-weighed syringe was left to deliver the mixture for a specific period of time and then weighed again after delivery. In the second approach, the volume difference was obtained by recording the liquid volume before and after delivery. In the third approach, the analyte mixture was delivered into a pre-weighed tightly capped PTFE vial, which was then weighed after a specific period of time. The difference between the three methods was less than 1% for test time periods ranging from 1 h to 4 days. An average delivery rate of the standard mixture for all experiments was 42 $\mu\text{g}/\text{min}$. The standard *n*-alkane concentration in the sampling chamber was changed by simply adjusting the air flow rate, or by preparing a new standard mixture with different liquid concentrations.

The standard gas system (Figs. 1 and 2) was allowed to reach steady state after each alteration in gas concentration. The theoretical analyte concentration (in $\mu\text{g}/\text{l}$) for each *n*-alkane (C_{alk}) in the sampling chamber was determined using the following equation:

$$C_{\text{alk}} = \frac{Q_{\text{alk}} m_{\text{alk}}}{Q_{\text{air}} m_{\text{total}}} \quad (1)$$

where Q_{alk} is the *n*-alkane delivery rate ($\mu\text{g}/\text{min}$), Q_{air} the air flow rate (l/min), m_{alk} the mass of *n*-alkane of interest in injected mixture (μg), and m_{total} is the total mass on *n*-alkane mixture injected (μg).

2.5. Ozone generation

Ozone was generated using a flow-through bulb with corona discharge. The efficiency of ozone generation was controlled by the dc voltage, temperature of the bulb, and the oxygen flow rate [36]. The voltage ranged from 11,400 to 5000 V, the temperature around the bulb was maintained between -35 and -80 $^{\circ}\text{C}$, and the oxygen flow rate was varied between 60 and 250 ml/min. Generated concentrations were as low as 10 ppbv and as high as 6400 ppmv [36].

2.6. Air flow and air relative humidity

Air flow rates were controlled by Sidetrack mass flow controllers (Sierra Instruments, Monterey, CA, USA) placed on both the primary and the dilution loops for each standard gas generator. Actual air flow rates were verified using a NIST-traceable primary gas flow standard, the mini-Buck calibrator (A.P. Buck, Orlando, FL, USA). Wide ranges of concentrations for formaldehyde, *n*-alkanes and other VOCs/semi-VOCs were obtained by adjusting both air (or nitrogen) flow rates and permeation cylinder temperature. The relative humidity was adjusted using an in-line impinger trap (Supelco, Oakville, Canada) and measured with a digital humidity meter (Canadawide Scientific, Ottawa, Canada). Relative humidities of 47 and 75% were obtained by maintaining the water level in the impinger trap at 1 and 8 cm height, respectively [29]. This impinger could be mounted at several points within the system.

2.7. Sampling chambers for SPME

Sampling chambers were constructed and installed downstream from the standard gas generators [34]. A schematic of an individual sampling chamber is provided in Fig. 2. These sampling chambers facilitated a steady-state mass

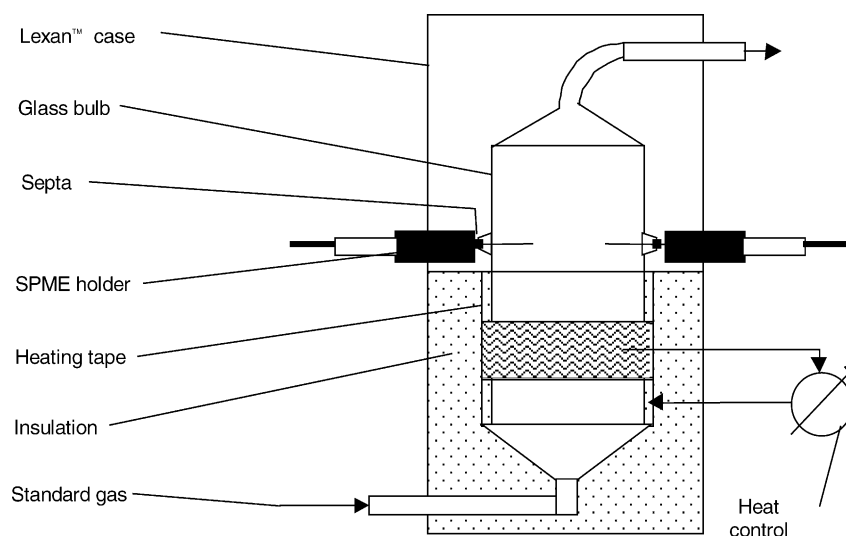


Fig. 2. Schematic of sampling chamber for SPME extractions.

flow of all VOCs and semi-VOCs, at constant temperatures. Each sampling chamber consisted of a custom made 1.5 l glass bulb with several sampling ports that were plugged with half-hole type Thermogreen LB-1 septa (Supelco, Mississauga, Canada). Omega 120 W heating tape was wrapped around the glass bulb to control temperature inside the bulb. An Omega K-type thermocouple was attached to the outside surface of the glass bulb. Both the heating tape and thermocouple were connected to an electronic heat control device constructed by the Electronics Science Shop at the University of Waterloo (UW). Air temperatures in the vicinity of the SPME fibers were maintained within $\pm 1.2\%$ ($\pm 0.3^\circ\text{C}$ at room temperature). Standard gas flow rates ranged from 50 to 3000 ml/min, resulting in mean air velocities inside the glass bulb of less than 10 mm/s. Standard gas generators and sampling chambers were validated using both SPME fibers, and ORBO adsorbent tubes combined with A.P. Buck I.H. personal air pumps for conventional NIOSH methods [37].

2.8. Air velocities

Air velocity can affect sampling/extraction rates for samplers using open bed geometry. To study this, a special air sampling system, consisting of a long glass cylinder with four different diameters (Glass Shop, University of Waterloo, Canada) was constructed and installed downstream from the standard gas generator (Fig. 1). The standard gas flow rate varied from 1000 to 4000 standard cubic centimeter per minute (sccm) to generating a wide range of air velocities at each diameter. Each section of the cylinder was equipped with sampling ports that were fitted with a half-hole Thermogreen septum (Supelco, Oakville, Canada) for easy insertion of an SPME fiber for sample collection at a controlled air velocity. In addition, a 1 l glass sampling bulb (Supelco, Oakville, Canada) was mounted downstream for static (no forced air flow) extractions. The average air velocities were calculated by dividing the air flow rate by the cross-section area of each stage of the sampling cylinder (Fig. 2). The average air velocities ranged from 0.2 to 83 cm/s depending on the sampling port location, and the standard gas flow rate [29]. This bulb could be mounted in several locations within the system.

2.9. Validation of standard gas concentrations for BTEX obtained with permeation tubes

The standard NIOSH-1501 sampling and analysis method was used to validate concentrations of standard gases in the standard gas mixture [37]. A portable I.H. air-sampling pump and a mini-Buck air flow rate calibrator (A.P. Buck I.H., Orlando, FL, USA) and ORBO 32SM charcoal tubes (Supelco, Mississauga, Canada) were configured to sample standard gas mixture containing the target VOCs. The standard gas system (Figs. 1 and 2) supplied the same VOC air mixture for both NIOSH and SPME sampling. The front

opening of the charcoal tube was placed in the outlet of the exhaust, downstream from the SMPE sampling chamber. The sampling time for the NIOSH-1501 method was 2 h. After sampling, the front and back sections of each charcoal tube were transferred into two clean 4 ml sample vial. Each vial was spiked with 1 ml of carbon disulphide (CS_2) and treated for at least 30 min with occasional agitation. Aliquots of 1 μl of the VOC samples were then analyzed on a Varian 3400 GC–flame ionization detection (FID) system.

SPME sampling with the 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) coating was 1 min. This time was enough to extract detectable amounts of analytes. The air flow rate through the standard gas sampling chamber was set to 2000 sccm. The VOC permeation tubes were incubated at 40°C . Air sampling was carried out at the ambient temperature of 23°C , and under the ambient pressure of 733 mmHg (1 mmHg = 133.322 Pa). Each SPME sample was analyzed on a portable SRI 8610C GC system.

2.10. Validation of standard gas concentrations obtained with syringe pump injections

The concentrations of C_5 – C_{15} *n*-alkanes in air from the standard gas generating device were verified by following the NIOSH-1550 method for the determination of airborne hydrocarbons [37]. A mass flow controlled I.H. air sampling pump (A.P. Buck) was used to draw air through an ORBO-32 charcoal tube placed at the outlet port of the SPME sampling chamber. The pumping flow rate was set to 100 ml/min, and it was calibrated with a A.P. Buck primary flow calibrator. The total sampling time was 8 h for the NIOSH method. The total sampling for the 100 μm PDMS fiber was only 2 h, i.e., long enough to achieve SPME fiber-gas partition equilibrium conditions for $\text{C}_{15}\text{H}_{32}$. Following the sample collection, the front and back portions of the used charcoal tube were transferred into two clean 4 ml vials, where *n*-alkanes were chemically desorbed from the charcoal with 1 ml CS_2 . All air samples were collected in quadruplicate. Five point GC calibration curves were generated for each of the *n*-alkanes. Calibration standards were prepared by spiking known amounts of *n*-alkanes into an equal mass of charcoal, followed by chemical desorption with CS_2 in 4 ml vials, and direct injections to GC. The adsorbed mass of each *n*-alkane in a sampling tube was determined by comparing the FID response to calibration curves. Finally, the air concentration for each *n*-alkane of interest was obtained by dividing the mass of *n*-alkane by the total volume of air that passed through the charcoal tube. Both SPME and the NIOSH samples were collected in quadruplicate.

3. Results and discussion

The standard gas system for development, testing, and validation of conventional, SPME-based, and other novel

Table 1
Applications of gas standard generators and sampling systems

Generation of standard gas concentrations for groups of VOCs, semi-VOCs, and ozone
Generation of standard gas concentrations for mixtures of VOCs and semi-VOCs
SPME fiber and sorbent tube selection studies
Development of SPME and sorbent tube extraction curves
Determination of SPME fiber/gas partition coefficients (K_{fg}) for individual analytes
Determination of uptake rates (K') for SPME-based time-weighted average sampling
Estimation of method detection limits
Studies of competitive adsorption for porous (solid) SPME fibers and sorbent capacity
Determination of air velocity effects on SPME extractions
Studies of air temperature and humidity on SPME extractions
Determination of ozone effects on SPME and sorbent tube extractions
Determination of sample recovery for SPME fibers and sorbent tubes
Determination of physicochemical characteristics of VOCs and semi-VOCs with SPME
Validation of SPME air sampling with sorbent tube-based air sampling methods
Daily QA/QC tests of analytical instruments using SPME samples of a gas standard

air sampling methods was designed, built, and tested. The system was also used as a day-to-day source of standards for quality assurance/quality control checks for analytical instrumentation including several gas chromatographs and mass spectrometers. The main functions and applications of this system are summarized in Table 1.

Table 2

Comparison of BTEX concentrations in standard air (in ppbv) measured using 65 μm PDMS–DVB and charcoal tubes

	Benzene		Toluene		Ethylbenzene		<i>p</i> -Xylene	
	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH
Measured average	62	62	19	18	4.7	5.2	3.8	4.0
S.D.	1.0	3.1	0.7	1.1	0.2	0.4	0.2	0.7
R.S.D. (%)	1.6	5.0	3.8	6.3	3.9	7.1	4.8	19
Theoretical ^a	64	64	21	21	4.1	4.1	4.8	4.8

^a Based on permeation rates and measured air flow rates. The SPME and the NIOSH values are based on $n = 5$ samples. Sampling time for SPME = 1 min; sampling time for the NIOSH 1501 = 2 h.

Table 3

Comparison of measured standard *n*-alkane concentrations using SPME fibers and NIOSH-1550 method

<i>n</i> -Alkane	Theory ($\mu\text{g/l}$) (at NTP)	SPME ($\mu\text{g/l}$) (at NTP)	NIOSH ($\mu\text{g/l}$) (at NTP)
Pentane	57.0	47.4	49.6
Hexane	38.5	31.7	39.1
Heptane	15.5	13.55	15.7
Octane	8.51	7.92	8.43
Nonane	4.09	3.94	4.27
Decane	2.01	1.95	1.84
Undecane	1.03	0.99	0.89
Dodecane	0.53	0.49	0.42
Tridecane	0.26	0.24	0.20
Tetradecane	0.13	0.11	0.10
Pentadecane	0.076	0.074	0.063

Note: Entries under “Theory” column signify theoretical estimation of concentrations determined from known masses in the standard, delivery rate and the diluent flow rate. NTP: normal temperature and pressure.

3.1. Validation of standard gas concentrations generated with permeation tubes

A comparison of the results for sampling with the 65 μm PDMS–DVB coating and charcoal tubes is presented in Table 2. The measured concentrations of target VOCs in standard air were close to each other and to the theoretical concentration obtained from the periodical measurements of emission rates associated with the permeation tubes and the actual air flow rate through the sampling chamber. Compared to the conventional charcoal tube method, the SPME air sampling combined with analysis on a portable GC was much faster and simpler, reducing the total sampling and analysis time from 24 h to less than 15 min.

3.2. Validation of standard gas concentrations generated with syringe injection

A comparison of theoretical *n*-alkane concentrations in standard gas estimated using Eq. (1) with those measured using 100 μm PDMS fiber and the NIOSH-1550 method is presented in Table 3. Both the NIOSH method 1550 and air sampling with SPME-based results were close to the theoretical concentrations; however, it should be noted that the SPME-based concentrations were at least as precise as those based on the NIOSH method. In all cases, the relative standard deviation (R.S.D.) associated with the SPME sampling were lower than those related with the NIOSH sampling, more than likely due to fluctuations in the pump flow rate

and possibly problems with the charcoal tubes. These points only additionally emphasize the complex nature of air sampling with a pump drawing air over a bed of charcoal in relation to the elegant approach of air sampling with SPME where in the latter case there are no moving parts and all of the analyte sorbed with the SPME coating are delivered directly to the instrument for analysis.

While the SPME sampling was very repeatable, particularly for the semi-volatile range of compounds the VOCs were not very stable with the PDMS coating. A fraction of these analytes was lost from the fiber in the time period between sampling and introduction to the GC system, but the problem was readily addressed. The losses of volatile compounds to air before desorption in the GC may explain the slightly higher variations observed for these compounds; however, no method is currently available for the estimation of TVOCs in air using adsorptive SPME coatings.

4. Conclusions

The standard gas system described in this paper proved to be very useful in generating standard gas concentrations for a wide variety of experiments involving SPME and other, conventional techniques used to validate SPME. The system was flexible to combine flows from three standard gases and to condition the standard gas. The major convenience of this system was the continuous availability of the standard gas which, besides the use in experiments, was used to (1) check the performance of the standard gas system, and (2) daily quality assurance/quality control runs on several gas chromatographs. The major consumables were the NIST-traceable permeation tubes which typically last several months; however, permeation tubes can be made from PTFE tubing and, with care and stringent quality control/quality analysis (QC/QA) protocol, will perform as well as commercial tubes. The syringe pump was convenient when several syringe refills were made ahead of time. Considering our experience with syringe pumps, we preferred permeation tubes. Permeation tubes can provide a desired emission rate as described elsewhere [3]. The standard gas generating systems presented in this paper permitted the study of the physical–chemical properties of various SPME systems and concepts for air sampling. The flexibility of the system enabled researchers to study a number of complex variables encountered in air sampling, such as rapid modifications to gas temperature, relative humidity, ozone concentrations, and most importantly the wide range of airborne organics in large concentration ranges.

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