Technical Notes

Microwave-Assisted Generation of Standard Gas Mixtures

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Microwave heating was employed for preparation of the standard gas of volatile organic compounds (VOCs) and semivolatile organic compounds (semi-VOCs) by using a 1000 W commercial domestic microwave oven and 1 L gas-sampling bulbs. The VOCs investigated were benzene, chloroform, 1,3-dichlorobenzene, tetrachloroethylene, toluene, and 1,1,2-trichloroethane, and the semi-VOCs used were the polychlorinated biphenyls (PCBs) PCB 1016 and PCB 1248. Since these weakly or nonpolar molecules are very poor absorbers of microwave energy, an appropriate amount of water was introduced to accept microwave radiation and act as the thermal source to accelerate their evaporation. The glass bulb may also contribute thermal energy to the VOCs/ semi-VOCs by accepting microwave energy to a small degree. For 0.5 μL of liquid VOCs on 10 mg of glass wool, it was shown that 15 μL of H_2O and 60 s of microwave heating yielded a very efficient evaporation [97.2−106.4%, compared with a classic method (Muller, L.; Gorecki, T.; Pawliszyn, J. *Fresenius' J. Anal. Chem.* 1999, *364*, 610−616)]. For 1 μL of PCB solution (1000 μg/mL in hexane), 15 μL of H_2O and 90 s of microwave heating also provided a complete evaporation. The addition of water was particularly significant for microwave-assisted evaporation of PCBs because semi-VOCs are much more difficult to evaporate than VOCs. This developed microwave technique proved to be quite simple, powerful, rapid, accurate, and safe for the preparation of VOC/semi-VOC standard gas. Solid- phase microextraction combined with gas chromatography was used for the gas analysis.

As a fast, efficient, and reproducible method, microwave-assisted sample preparation has attracted significant attention from analysts in recent years.[1−5] The microwave apparatus is becoming a necessary instrument, joining spectrometers and chromatographs as laboratory-essential analytical instrumentation.[1] Microwave radiation is nonionizing, with insufficient energy to rupture chemical bonds, but sufficient energy to cause molecular rotation or movement of ions. These effects will in turn cause heating.[6] By using microwave heating, a series of methods and techniques have been developed for sample preparation in environmental organic analysis, such as microwave-assisted extraction, focused microwave-assisted Soxhlet extraction, microwave-assisted headspace analysis, microwave-assisted derivatization, microwave-assisted saponification, and microwave-assisted decomposition.[4] These novel techniques possess a lot of advantages over traditional methods, including increased efficiencies of sample preparation, savings of energy and time, and environmental friendliness.

Some researchers have employed microwave energy to enhance the evaporation of specific components from samples. Microwave drying is a well-known technique, with a long history in industrial use. It has also been used for analytical sample preparation as well as for moisture measurement.[7,8] Other similar techniques include microwave-assisted pervaporation [9,10] and the microwave- assisted headspace analysis mentioned above. The most recent use of microwave- assisted evaporation was reported by Link and Kingston[11] for the complete recovery of volatile species of inorganic trace analytes to improve inductively coupled plasma mass spectrometry (ICPMS) analysis.

Preparation of standard gas mixtures of the target compounds is generally necessary for pursuing quantitative calibration in air analysis. It is also very important for modeling the investigation of the environmental fate and transport of persistent organic pollutants. In our laboratory, several methods for the generation of a gas mixture of volatile organic compounds (VOCs) have been investigated previously based on the use of a syringe pump

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delivery system,[12] a Kin-Tech standard gas generator (Kin-Tech, La Marque, TX) and National Institute of Standards and Technology (NIST) traceable certified permeation tubes (Kin-Tech),[13] and Supelco gas-sampling bulbs (Bellefonte, PA).[14] Each method has its merits. However, when syringe pump delivery or the Kin-Tech standard gas generator and NIST traceable certified permeation tubes are used for standard gas preparation, a long time is required both for the systems to reach equilibrium and for the quantitative calculation of VOC concentrations based on the amount of evaporated VOCs, while with the Supelco gas-sampling bulb a 10 min heating procedure at 100 °C is needed as described in the literature. Therefore, it is desirable to develop novel methods to simplify the preparation of standard gas mixtures of VOCs. Moreover, because of the lower vapor pressure of semi-volatile organic compounds (semi-VOCs), preparation of the standard gas of this kind of compound is generally inconvenient. Thus, finding a simple and powerful means for the generation of the standard gas for semi-VOCs is especially attractive.

In this paper, the method using microwave energy for the generation of standard gas mixtures of several VOCs and polychlorinated biphenyls (PCB 1016 and PCB 1248), a class of semi-VOCs, was established. Solid-phase microextraction (SPME) was used for VOC/semi-VOC sampling coupled with GC-FID/ECD determination.

EXPERIMENTAL SECTION

Chemicals. Six VOCs, benzene, chloroform, 1,3-dichlorobenzene, tetrachloroethylene, toluene, and 1,1,2-trichloroethane, were purchased from Aldrich. All were 99% purity. A VOC mixture was obtained by mixing equivalent volumes of the six VOCs. Semi-VOCs PCB 1016 and PCB 1248 were purchased from Restek, 1000 μg/mL in hexane.

Procedure of Microwave-Assisted Generation of the Standard Gas of VOCs/Semi-VOCs. A commercial domestic microwave oven (1000 W, model MW5490W, Samsung, Korea) and 1 L gas-sampling bulbs (Supelco, Bellefonte, PA) were used for standard gas preparation. The inner walls of the glass bulbs were deactivated by silanization, and the bulbs were sparged with nitrogen before use. A new piece of glass wool (about 10 mg) was set inside the sampling port of the bulb each time and was moistened with pure water (15 μL). The port was then sealed with a Teflon- faced silicon rubber septum through which a small aliquot of the liquid standard VOC mixture (0.5 μL) or PCB standard solution (1 μL) was injected onto the glass wool (Figure 1a). Finally, the bulb was placed in the microwave oven to receive microwave radiation for a certain time. The microwave output was always set at power level 0 (100%).

Procedure of SPME and GC-FID Analysis of VOCs/Semi-VOCs. After the bulb was cooled to room temperature, a commercial SPME device (Supelco) equipped with a poly(dimethylsiloxane) (PDMS) fiber (coating thickness 100 μm) was used for sampling the VOC/semi-VOC gas mixtures from the bulb through the septum (Figure 1b). The fiber was exposed to the standard gas in the bulb under static conditions and then
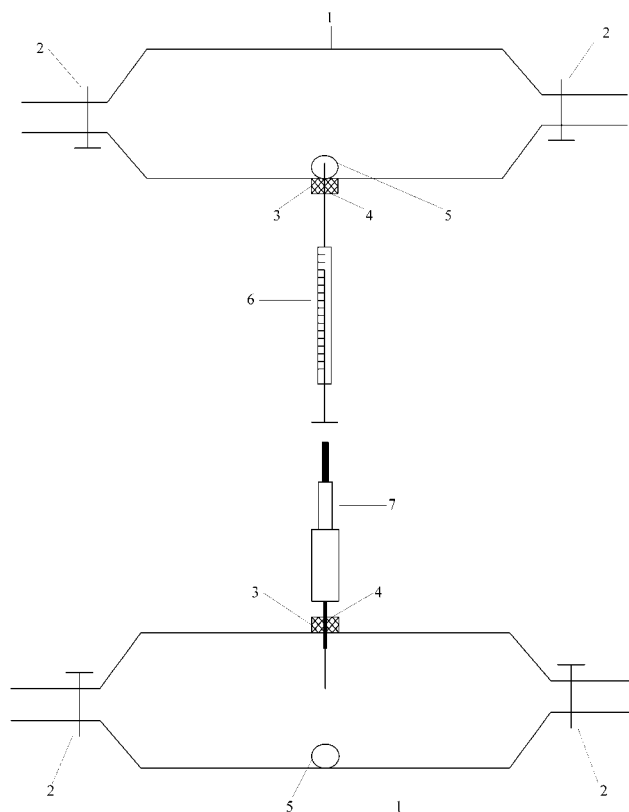
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Figure 1. Schematic of the gas-sampling bulb used for microwave-assisted standard gas preparation: (a, top) addition of water and standards in organic solvent onto glass wool inside the bulb before microwave heating, (b, bottom) SPME sampling of the standard gas from the bulb after microwave heating, (1) Supelco gas-sampling bulb body, (2) valves (stopped), (3) port, (4) Teflon-faced silicon rubber septum, (5) glass wool, (6) syringe, (7) SPME device.

transferred to the GC injector. Extraction times were 3 min for VOCs and 5 min for PCBs.

A Varian model 3400 GC equipped with an SPB-5 capillary column (30 m × 0.25 mm, 1 μm df) from Supelco was employed for gas analysis. For VOC analysis, a flame ionization detector (FID) was used and hydrogen was selected as carrier gas at 30 psi. The column was programmed as follows: 40 °C initial, hold for 1 min, ramp to 100 °C at 15 °C/min, and hold for 1 min. The detector was maintained at 280 °C, and the PDMS fiber was desorbed for 1 min at 250 °C. For PCB analysis, an electron capture detector (ECD) was employed and helium was used as carrier gas at 15 psi. The column was ramped from 150 to 300 °C at 4 °C/min and held for 5 min. The detector was held at 300 °C, and the fiber was desorbed for 3 min at 250 °C.

RESULTS AND DISCUSSION

Transport of Thermal Energy from Media to VOCs/Semi-VOCs during Microwave Heating. The VOCs and semi-VOCs investigated are weakly or nonpolar molecules, so they are inefficient at absorbing microwave energy. To use microwave heating to prepare the standard gas of VOCs/semi-VOCs, it is essential to introduce a suitable medium to accept microwave energy and then transfer the thermal energy to the VOCs/semi-VOCs to facilitate their evaporation.

Water is an efficient absorber of microwave energy and is the cheapest and most environmentally friendly solvent used in

Table 1. Effect of Microwave Heating Time on the Generation of Standard Gas Mixtures of Volatile Organic Compounds[a]

compd	bp (°C)[b]	without MH[c]		with MH, 30 s[c]		with MH, 60 s[c]		with MH, 90 s[c]	
		PA (%)	RSD (%)	PA (%)	RSD (%)	PA (%)	RSD (%)	PA (%)	RSD (%)
benzene	80.1	79.5	3.4	93.1	3.6	106.4	4.2	103.8	2.9
chloroform	61.7	85.3	3.8	97.8	2.2	104.2	3.1	105.5	4.3
1,3- dichlorobenzene	172.0	69.5	4.5	86.2	4.9	97.2	7.5	95.4	5.6
tetrachloroethylene	121.1	72.4	2.8	89.5	7.4	103.1	6.3	105.6	3.0
toluene	110.8	76.7	4.1	90.7	5.8	99.5	5.9	96.7	4.8
1,1,2- trichloroethane	113.5	74.6	3.4	92.2	5.1	98.7	7.5	99.9	4.1

[a] Sample, 0.5 μL of VOC mixture; water added, 15 μL; total time for adding sample, microwave heating, and then cooling to room temperature, 8 min; number of parallel experiments, $n = 3$. The results are presented as a percentage of the chromatographic peak area obtained with the conventional method (evaporation by heating in a conventional oven at 100 °C for 10 min). [b] Cited from ref 16. [c] MH = microwave heating, PA = chromatographic peak area.

Table 2. Effect of Microwave Heating Time on the Generation of Standard Gas Mixtures of PCBs[a]

compd	without MH[b]		with MH, 60 s[b]		with MH, 90 s[b]		with MH, 120 s[b]	
	PA (%)	RSD (%)	PA (%)	RSD (%)	PA (%)	RSD (%)	PA (%)	RSD (%)
PCB 1016	29.4	5.2	94.5	4.6	115.6	3.7	114.4	4.2
PCB 1248	26.2	6.1	91.2	3.2	112.3	2.5	113.7	4.9

[a] Sample, 1 μL of PCB standard solution; water added, 15 μL; total time for adding sample, microwave heating, and then cooling to room temperature, 8 min; number of parallel experiments, $n = 3$. The results are presented as a percentage of the chromatographic peak area obtained with the conventional method (evaporation by heating in a conventional oven at 100 °C for 10 min). [b] MH = microwave heating, PA = chromatographic peak area.

chemical laboratories. Therefore, water was selected as the medium to accept microwave energy and then to prompt the evaporation of VOCs/semi-VOCs. Glass wool was used to support both water and VOC/semi-VOC liquids, allowed a close contact between the aqueous and organic phases, and hence led to an efficient transport of thermal energy from water to VOCs/semi-VOCs.

For standard gas preparation, pure VOC liquids were used directly but PCB standard solutions instead of pure PCBs were chosen. Since the vapor pressures of semi-VOCs are much lower than those of VOCs, only a very small amount of neat semi-VOCs can be evaporated in the 1 L bulb. To transport such a small amount of PCBs into the bulb quantitatively and conveniently, the diluted solutions of semi- VOCs are obviously preferable. However, these PCB standard solutions were also poor absorbers of microwave energy because their solvent hexane is also a nonpolar compound.

In the absence of water, glass wool, and VOCs/semi-VOCs, the glass bulb itself becomes hot after radiation in the microwave oven (the bulb wall's temperature was about 45 °C after 60 s of microwave heating). This indicates the bulb can also accept microwave energy to a certain degree and therefore is another medium that contributes thermal energy conversed from microwave energy, supporting the evaporation of VOCs/semi-VOCs. However, the glass wool is a very poor absorber of microwave energy.

Optimization of Conditions for Microwave-Assisted Generation of Standard Gas Mixtures of VOCs/Semi-VOCs. It was found that 0.5 μL of VOC mixture (liquid) evaporates inefficiently in the 1 L bulb after 8 min at room temperature (Table 1). 1,3-Dichlorobenzene is not as volatile as the other five compounds because its boiling point is the highest among the six VOCs. Their

boiling points range from 61.7 °C (chloroform) to 172 °C (1,3-dichlorobenzene).

In all cases evaporation of VOCs was enhanced by microwave heating, especially for 1,3-dichlorobenzene. The addition of a proper amount of water to the bulb could still accelerate their evaporation. It was shown that 60 s of microwave heating yielded a very efficient evaporation (97.2–106.4%) for the six VOCs when 15 μL of pure water and ca. 10 mg of glass wool were used. However, it was observed from the SPME–GC results that a negative effect resulted when too much water was added to the system (Table 3). This may be due to the deterioration of SPME efficiency caused by too much moisture in the bulb. It is known that high moisture (>90% RH) will affect the SPME efficiency.[15]

PCB evaporation is quite slow at room temperature. It may be promoted by microwave heating, especially when a proper amount of water is added to the system. The presence of water proved to be very important for this microwave- assisted evaporation of PCBs. For 1 μL PCB solutions (1000 μg/mL in hexane), 90 s of microwave heating yielded an efficient evaporation in the presence of 15 μL of water, 15.6% higher than the result obtained by 10 min of heating at 100 °C using a conventional oven. In the absence of water, the efficiency of microwave-assisted evaporation of PCBs was obviously reduced to a level even less than that obtained using a conventional oven (Tables 2 and 4).

The efficiency of microwave-assisted evaporation is presented as a percentage of the chromatographic peak area obtained with the following method.[14] Standard solutions were injected into a 1 L Supelco bulb. The bulb was next heated in a conventional oven

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Table 3. Effect of Water Addition on the Efficiency of Microwave-Assisted Generation of Standard Gas Mixtures of Volatile Organic Compounds[a]

compd	0 μL of water		5 μL of water		15 μL of water		50 μL of water	
	PA (%)[b]	RSD (%)	PA (%)[b]	RSD (%)	PA (%)[b]	RSD (%)	PA (%)[b]	RSD (%)
benzene	94.3	6.4	99.4	3.2	106.4	4.2	92.7	2.9
chloroform	97.2	4.1	101.5	2.4	104.2	3.1	96.4	3.6
1,3- dichlorobenzene	89.5	4.8	92.2	3.7	97.2	7.5	87.6	4.5
tetrachloroethylene	90.3	3.6	96.8	5.8	103.1	6.3	93.4	2.4
toluene	92.6	3.9	97.4	6.1	99.5	5.9	90.5	4.7
1,1,2- trichloroethane	93.0	2.5	95.6	4.5	98.7	7.5	89.5	5.8

[a] Sample, 0.5 μL of VOC mixture; microwave radiation time, 60 s; total time for adding sample, microwave heating, and then cooling to room temperature, 8 min; number of parallel experiments, $n = 3$. The results are presented as a percentage of the chromatographic peak area obtained with the conventional method (evaporation by heating in a conventional oven at 100 °C for 10 min). [b] PA = chromatographic peak area.

Table 4. Effect of Water Addition on the Efficiency of Microwave-Assisted Generation of Standard Gas Mixtures of PCBs[a]

compd	0 μL of water		5 μL of water		15 μL of water		50 μL of water	
	PA (%)[b]	RSD (%)	PA (%)[b]	RSD (%)	PA (%)[b]	RSD (%)	PA (%)[b]	RSD (%)
PCB 1016	81.2	2.5	93.5	4.1	115.6	3.7	92.7	3.1
PCB 1248	79.3	3.7	91.2	2.9	112.3	2.5	90.5	4.6

[a] Sample, 1 μL of PCB standard solution; water added, 15 μL; total time for adding sample, microwave heating, and then cooling to room temperature, 8 min; number of parallel experiments, $n = 3$. The results are presented as a percentage of the chromatographic peak area obtained with the conventional method (evaporation by heating in a conventional oven at 100 °C for 10 min). [b] PA = chromatographic peak area

at 100 °C for 10 min. After cooling, the SPME−GC system mentioned above was employed for gas analysis.

Advantages and Limitation of Microwave-Assisted Generation of Standard Gases. The advantages of microwave-assisted generation of standard gases include the following.

(1) It is simple: Both the device and operation are uncomplicated, and the concentration of the standard gas is easily controlled by changing the amount of liquid VOC or semi-VOC solution added to the bulb.

(2) It is powerful: Not only VOCs but also the semi-VOCs PCBs could efficiently evaporate with a microwave radiation for 60−90 s.

(3) It is rapid: A cycle of preparation of standard gas, from adding sample to the bulb to accepting microwave radiation and then to cooling the bulb to room temperature, can be completed in 8 min.

(4) It is accurate and precise: The microwave heating provides an efficient evaporation of VOCs/semi-VOCs, and the Supelco gas-sampling bulb stays airtight during and after microwave heating since the temperature of the bulb's wall is just about 45 °C through 60 s of microwave heating. These ensure the preparation of VOC/semi-VOC gas mixtures is accurate and precise. Moreover, it was found that the standard gas was stable for more than 24 h after preparation.

(5) It is safe: The procedure of microwave heating is very easily controlled. Moreover, the temperature of the tube itself and the pressure in the bulb are not very high.

(6) It is inexpensive: It was proven that one bulb of the standard gas could be used several times for SPME sampling, and this did not cause obvious differences among the results. Moreover, microwave heating is much more energy-saving than traditional heating.

The main limitation of the microwave-assisted generation of standard gas is that it is not a flow-through system.

CONCLUSION

By exploiting thermal energy transport from microwave-absorbable media to VOCs/semiVOCs, weak or nonpolar materials could be efficiently evaporated by microwave radiation. Thus, a simple, powerful, rapid, accurate, and safe method for preparation of the standard gas of VOCs/semi-VOCs was established for air analysis. Particularly, due to the use of commercial domestic microwave ovens, this microwave-assisted technique may be conveniently introduced into laboratory protocol as an alternative to traditional methods for its merits.