Development of a Hollow Waveguide Sampler for Detection of Chlorinated Aromatic Compounds in Soils

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In this paper, a Fourier transform infrared (FT-IR) spectroscopic method for detection of chlorinated aromatic compounds in soils was developed. The sensing device of this method was based on an infrared hollow waveguide, the inner surface of which was coated with a hydrophobic film. Vaporized chlorinated aromatic compounds from soils were trapped onto the hydrophobic film of the hollow waveguide sampler following detection by FT-IR spectrometry. The extraction process in this method was similar to the headspace solid-phase microextraction (HSSPME) in principle. Means of increasing the speed of transfer of the vaporized organic species to the sampler were also studied. Results indicated that, with a negative pressure on the end of the sampler, the speed of transfer increased significantly. Vapor pressures of the analytes were used as an indication to test the limitation of this method in the analysis of organic compounds in soils. Results showed that analytes with vapor pressures lower than 12 Torr could be detected quantitatively. The typical R-square of the regression on the concentration and IR signals was around 0.99 and the typical detection limits were in the range of hundreds of parts per billion.

Chlorinated aromatic compounds are commonly found contaminants in environmental soil samples. For example, chlorobenzenes have been listed as priority pollutants and can be found in various matrixes such as water, soils, sediments, and sewage sludges. Polychlorinated biphenyls (PCBs) are probable human carcinogens but have been applied in large doses in various industrial products. Analysis of these compounds in solid matrixes, such as soils and sediments, requires several steps in extraction and preconcentration of the analytes in the conventional methods, i.e., Soxhlet extraction. In recent years, several extraction methods have been applied to solid samples to reduce the use of organic solvents and increase the speed of analysis, for example,

supercritical fluids extraction, 6,7 accelerated solvent extraction, 8 and subcritical fluid extraction.^{9,10} To reduce the equipment cost and the analysis time in the extraction process and sample preconcentration, the solid-phase microextraction method was proposed by Pawliszyn and co-workers. 11-13 Since then, great applications in the analysis of organic compounds in aqueous solutions have been reported, such as in the analysis of aromatic hydrocarbons, 14,15 halogenated volatile organic compounds, 16,17 polyaromatic hydrocarbons, 18,19 polychlorinated phenyls, 18 pesticides, ^{20,21} nitroaromatic compounds, ²² and phenols. ²³ Basically, the SPME method utilizes a fine fused-silica fiber coated with a polymer to extract organic compounds from their matrix. An SPME fiber combines the sampling and preconcentration in a single step. After sampling, the adsorbed analytes were desorbed from the fiber and analyzed by gas chromatography (GC) or highperformance liquid chromatography. However, the SPME method, in analysis of organic compounds in soil, is not as widespread as in water. To extend SPME method to solid samples, the headspace solid-phase microextraction (HSSPME)24-27 method was developed in recent years. The sampling of organic species was

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performed on the headspace of the samples. Both liquid and solid samples can be used by this method. There are several advantages to this HSSPME method, including shorter extraction time and its application to any type of matrix. ^{24,26} However, some difficulty was found in the examination of volatile compounds in the trapping of the vaporized compounds onto the SPME phase. For low-volatility compounds, thermal desorption of the analytes from the solid matrix or addition of modifiers to the soil should be applied.

Unlike the SPME/chromatographic method, the Fourier Transform Infrared (FT-IR) spectroscopic method can provide the advantages of direct analysis, spectral selectivity, and speedy analysis of organic compounds. Use of the principle of attenuated total reflection (ATR), in conjunction with a Fourier Transform Infrared (FT-IR) spectrometer, in sensing organic compounds in aqueous solutions²⁸⁻³² can easily overcome the limitation of the conventional IR method in handling aqueous solutions. Improvements of sensitivities were approached by the combination of the principle of SPME with the ATR/IR method. Examples of the detection of volatile organic compounds (VOCs), 33,34 nitrobenzene,35 and others66 in aqueous solutions can be found in the literature. Because the SPME-ATR/IR method is a direct sensing method, the SPME phase should exhibit low IR absorptivity. This limits the use of the common SPME phase in the SPME/ chromatographic method, such as poly(dimethylsiloxane) or polyacrylate. Several commonly used polymers, such as lowdensity polyethylene,34,36 poly(vinyl chloride),34 and polyisobutylene,37 which exhibit low IR absorptivity in the region lower than 1000 cm⁻¹, were typically used in the detection of chlorinated compounds in SPME-ATR/IR methods. Gobel et al.37 compared several coated polymers for the SPME-IR/ATR method and found that PIB is the most suitable SPME phase in detection of trace chlorinated hydrocarbons in water. However, the SPME-ATR/IR method has not been applied to analysis of solid samples.

In this paper, we used the principle of HSSPME combined with the IR sensing method to extend the IR method to solid samples, i.e., soil. The IR sensing device in this paper is based on an IR hollow waveguide, the inner surface of which was coated with hydrophobic film and which served as the SPME phase. The vaporized organic sample from solid samples was adsorbed onto the SPME phase and can be sensed by an FT-IR spectrometer. The detail of this method will be described in the next section.

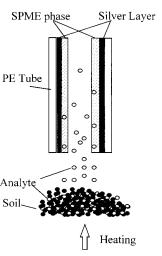


Figure 1. Schematic diagram of the principle of the HSSPME-IR method proposed in this work.

METHOD DEVELOPMENT

The basic principle of this method is shown in Figure 1. An IR hollow waveguide, its inner surface coated with SPME phase, is used to adsorb vaporized analytes from the soils. The adsorbed analytes inside the hollow waveguide can be detected by an FT-IR spectrometer. If the analytes adsorb to the SPME phase rapidly and analytes remain immobilized in the polymer phase, an IR signal with sufficient signal-to-noise ratio can be measured and the quantity of the analytes can be determined. Basically, the amount of analytes presented in the hollow waveguide should be related to the volatility of the analytes, the interaction between the solid matrix and analytes, and the adsorption efficiency of the SPME in the hollow waveguide. Therefore, three major steps in sampling can be recognized by this proposed method: (1) vaporization of analytes from the soil matrix to the headspace, (2) transfer of vaporized analytes from the headspace to the hollow waveguide sampler, (3) adsorption of the vaporized analytes onto the SPME phase of the sampler. In the first step, both the volatility of analytes and the interaction of analytes and soil matrix are equally important. The vapor pressure is an important indication of the volatility of the analytes, which can be easily obtained in some of the data books.^{38,39} Basically, the vapor pressure of analyte strongly affects the efficiency of the evaporation of analyte out of the soils. This vapor pressure of analyte can be increased by addition of thermal energy to the soil sample. The increase of temperature can also affect the escaping efficiency of analytes out of the soil matrix. Therefore, in this stage, addition of a large amount of thermal energy to the sample is preferred.

In the second step, the analytes in the headspace can create positive pressure inside the sample vessel. This pressure directs the vapor to pass through the hollow waveguide. Compared with the conventional HSSPME, the open end of the hollow waveguide can increase the speed of transferring the vaporized analytes to the SPME phase. Furthermore, the leaking problem in conventional HSSPME can be eliminated because the open end of the

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hollow waveguide sampler can release all the pressure built inside the sample vessel. However, the concentration of the analytes presented in the soil sample is typically lower than 10 ppm. This small amount of analyte can only create a small amount of vapor pressure inside the sample vessel. To increase the speed of transportation of analytes through the hollow waveguide, positive pressure can be added to the sample vessel or negative pressure on the end of the hollow waveguide. Although a purge of gas can form positive pressure to carry the vaporized analyte through the hollow waveguide sampler, the analytes are diluted and the linear flow rate of the analyte is also increased. The dilution of analytes reduces the force to partition onto the SPME phase, and the fast linear flow rate of the analyte can also reduce the time used to contact the SPME phase. Meanwhile, when the gas flow passes through the hollow waveguide, part of the adsorbed analytes can also be removed out of the hollow waveguide. Therefore, a more reasonable approach is to apply negative pressure on the end of the hollow waveguide. By suction with a pneumatic pump, the small negative pressure on the exit of the sampler can expedite the transfer of vaporized analytes in the headspace, but without the problems described above. Because the concentrations of analytes are typically lower than 10 ppm, the vapor pressure forming inside the sample vessel differs slightly when the concentration is varied. Therefore, the major driving force behind different concentrations of analytes passing through the hollow waveguide sampler will be the negative pressure produced by the suction device. Meanwhile, the suction device can be operated at a constant gas flow rate. Under this condition, the analytes will be exposed in the hollow waveguide for the same length of time. Hence, the adsorption efficiency will be similar for different concentrations of the analytes.

In the third step, several factors affect the amount of analytes that can be adsorbed and remain in the SPME phase of the IR hollow waveguide sampler. First, the partition coefficient of analytes between the SPME phase and the gas phase strongly affects the ability of analytes to adsorb onto the SPME phase. Second, if moisture is presented in the vapor, it has chances to block the surface of the SPME phase, leading to lower adsorption efficiency. Third, the temperature of the vapor passed through the waveguide influences the partition coefficient of the analytes. Basically, the vapor pressure of the analytes is very small because the concentration of the analytes in the typical examined sample is in the low part per million region. However, when soils contain moisture, the water vapor may form a flow through the hollow waveguide. This can seriously influence the IR signals because the water molecules may reduce the chance of vaporized analytes making contact with the SPME phase. If the temperature inside the hollow waveguide is low enough, water vapor may also condense on the surface of the SPME phase and block the SPME phase out of vaporized analytes. This reveals that an optimal temperature exists to compromise both effects. An important drawback is that the sampler was formed by a polyethylene (PE) tube, which can be distorted if heated at a temperature over a certain limit.

EXPERIMENTAL SECTION

Apparatus. The diagram of the setup in this work is shown in Figure 2. A two-neck reaction bottle (100 mL in volume) was

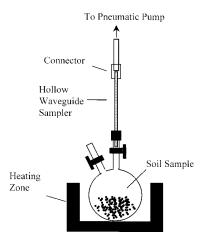
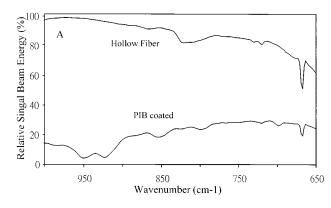


Figure 2. Schematic diagram of the setup of the HSSPME hollow-waveguide sampler.

used as an extraction chamber and was placed in a heating oven. A temperature controller was used to regulate the temperature of the heating zone. The hollow waveguide sampler was inserted into one neck of the extraction bottle. Polyethylene (PE) tubes, obtained from a local supplier, were used as the substrate of the hollow waveguide. The internal and external diameters of the PE tube were 1.5 and 2.2 mm, respectively. Details of the production of the hollow waveguide sampler were described in ref 40.

Materials and Reagents. Polyisobutylene (PIB) was obtained from Aldrich (Milwaukee, WI) and used as the SPME phase. Diethyl ether (TEDIA, Fairfield, OH) was used to dissolve PIB, and 1-chloronaphthalene (1-CN), chlorobenzene (CB), 2-chlorotoluene (2-CT), and trichloroethylene (TCE) were used as probe molecules for representing the different volatilities of chlorinated aromatic compounds which were obtained from Merck (Schuchardt, Germany). Soil was used as a solid matrix and was given as a gift from the department of soil science, National Chung-Hsien University (Taichung, Taiwan). The obtained soil (Clay loam) contained 24.7% sand, 36.1% slit, and 39.2% clay and was used without pretreatment. To ensure the cleanliness of the soil, soils were examined for their IR spectra in the IR regions of interest before being used as solid matrixes. No absorption bands were present in the spectral region of interest by the proposed method, which will be presented in the Results and Discussion. Represented semivolatile chlorinated compounds were dissolved in diethyl ether to form a 1.2% wt/vol solution. A certain amount of the formed solution was added to 10 g of soil and vigorously shaken in a sealed volumetric flask. The sample was further airdried for 30 min to remove the organic solvent.

Procedure of Sampling and Detection. After probe organic compounds were added to the soil samples to form the desired concentrations of analytes as described above, soil samples were placed into the two-neck round bottle. The sample bottle was placed into the heating oven. A pneumatic pump (Cole-Parmer Instrument Co., Niles, IL) was used to withdraw vaporized analytes through the sampler to increase the speed of transportation of vaporized analytes. The pneumatic pump was controlled to provide a gas flow rate of 5 mL/min. Two nonimaging infrared concentrators (modified from Spectral-Tech fiber probe accessory) were



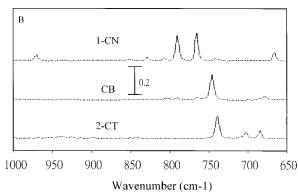


Figure 3. (A) IR single beam energy spectra of PIB-coated and noncoated hollow waveguide. (B) Typical IR spectra of 50 ppm of 1-CN, chlorobenzene, and 2-chlorotoluene. Spectra were 100 scans coadded at a resolution of 4 cm⁻¹.

placed at each end of the hollow waveguide sampler for concentrating IR radiation from the sample compartment of an FT-IR spectrometer to the hollow waveguide and to redirect the transmitted IR radiation back to the MCT detector. A Nicolet Magna 550 FT-IR spectrometer equipped with a medium-range mercury-cadmium-telluride (1 mm²) detector was used to detect the absorbed analytes. The typical energy spectra of a 5% PIBcoated and a noncoated hollow waveguide produced in this work are shown in Figure 3A. Each spectrum was obtained by co-adding 100 scans with 4 cm⁻¹ resolution. As can be seen in this figure, PIB has small absorption features in the region lower than 1000 cm⁻¹. This allows the application of this polymer to the detection of organic compounds in aqueous solution and makes it especially useful for the detection of halogenated compounds. Two small peaks located around 900 cm⁻¹ are used as an indication of the film thickness of the PIB coating. Typical spectra of the probe molecules measured by this method were also shown in Figure 3B. Two strong absorption peaks located around 700 cm⁻¹ can be found in the spectrum of 1-CN, and the peak located at 766 cm⁻¹ was selected as an indication of the amount of 1-CN being detected in this work. For CB and 2-CT, the peaks located around 750 cm⁻¹ were used. For regeneration of the sampler, a lowpressure air pump was used to purge the sampled hollow waveguide sampler to remove the adsorbed analytes. By pumping air flow through the sampler for 20 min, the signals of the probe molecules were completely removed. No significant change of the PIB absorption band intensity was observed after regeneration of the hollow waveguide sampler.

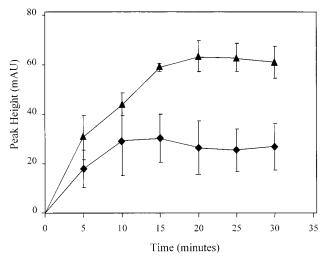


Figure 4. Time profiles for detection of 50 ppm 1-CN in dry soils. Two curves were plotted; the signals in 120 °C but without (u) and with (s) suction. The suction air flow rate was 5 mL/min. Each point was averaged from triplicate runs. One standard deviation was also shown for each point.

RESULTS AND DISCUSSION

Time profiles of IR signals will be related to the time to move organic compounds out of the solid matrix, which is related to both the heating temperature of the solid matrix and the volatility of the organic compound. Basically, strong IR signals can be obtained faster if there is weaker interaction between the solid matrix and the analyte. Also, speed in obtaining strong IR signals can be obtained if the analytes behave with high volatility. Furthermore, the efficiency to retain the adsorbed molecules in the SPME phase is also important to maintain the IR signals. To examine these effects, 50 ppm 1-CN in 10 g of dry soils were first examined for the IR signals in different evaporation (adsorption) time. The IR signals obtained when the temperature is kept at 120 °C are shown in Figure 4. Two curves can be seen in this plot, including with and without the pneumatic pump to withdraw the vaporized analytes. For runs without the pneumatic pump, the IR signals reached a maximum signal around 30 mAU after 10 min. For runs with the pneumatic pump, the IR signals increased to around 60 mAU and maintained a certain level. The fact that the IR signals maintained a certain level reveals that the 1-CN was immobilized (strongly adsorbed) in the PIB phase. The increase of the IR signals also reveals that the transportation of the vaporized analytes was more effective with the assistance of a pneumatic pump. Meanwhile, the relative standard deviation of detected IR signals without suction in the end is also higher than that of signals with negative pressure in the end. Therefore, negative pressure created by a pneumatic pump at 5 mL/min air flow rate was used for the remainder of the experiments.

Effect of Temperature. Temperature is an important factor in removing organic compounds from the solid matrix. Not only can high temperature increase vaporization of the organic analytes but it can also effectively assist the organic molecules in escaping from the solid matrix. To study the effect of temperature, 50 ppm 1-CN in dry soil samples were prepared and examined at five different heating temperatures. Figure 5 shows the IR signals obtained after 10 minutes of evaporation/adsorption time. In these

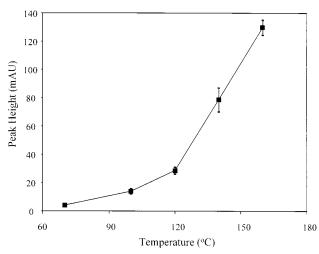


Figure 5. Plot of 50 ppm 1-CN signals at different heating temperatures. Spectra were 100 scans coadded at $4~\rm cm^{-1}$ resolution. Each point was averaged from triplicate runs. One standard deviation was also shown for each point.

experiments, the pneumatic pump was used to withdraw the vaporized molecules into the sampler. As can be seen in this plot, there were dramatically increased IR signals for a heating temperature higher than 120 °C. Basically, the heating temperature can increase the speed of evaporation of the analytes out of the soil matrix and into the headspace. The temperature plot in Figure 5 favors the situation of high temperature in analysis. However, considering the stability of the coated polymer phase in the sampler, the higher temperature can result in distortion of the hollow waveguide sampler. In our observation, when temperatures were higher than 160 °C, the lifetime of the hollow-waveguide sampler decreased tremendously. To compromise, the heating temperature should be lower than 160 °C.

Effect of Moisture. A soil sample usually contains a small amount of water. Basically, water in the soil can affect the detected signals in two ways. First, the water molecules can interact with active sites of soils and release the organic compounds. Second, the water vapor pressure is different for soils with different water content. The forming water pressure can affect the flow rate of the vaporized organic compounds through the hollow-waveguide sampler. Meanwhile, the vaporized water molecules can be condensed on the surface of the SPME phase inside the hollow waveguide. To study the effect of water, 50 ppm 1-CN soil samples were added with 10 to 50% in weight of water. By keeping the heating temperature of the samples at 120 °C, the obtained IR signals plotted with evaporation/adsorption times were shown in Figure 6. As can be seen in Figure 6, for soil samples containing less than 25% water, the obtained IR signals were very similar in evaporation/adsorption times. According to the results of Santos et al.,26 the extraction efficiencies for three chlorobenzenes in soils were increased if a large amount of water was added to the soils. In their observation, increasing analyte signals were observed if water contents were lower than 50%. If water contents were higher than 50%, the analytical signals seemed independent of the water amount. These observations were also reported by Fromberg et al..²⁷ In our observed time profile of the analytical signals, the samples containing 10% and 25% water have very similar analytical

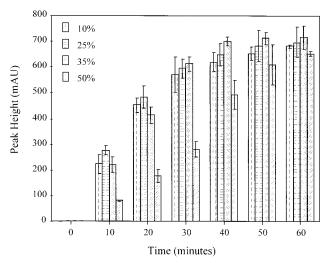


Figure 6. Detection time profiles of 50 ppm 1-CN in soils with different moisture content. Each point was averaged from triplicate runs. One standard deviation was also shown for each point.

signals, as can be seen in Figure 6. The IR signals at the first 20 min for soil samples containing 35% water are slightly lower than those for samples containing 10 or 25% water. However, the IR signals after 20 min for samples containing 35% water are slightly higher than those for samples containing 10 and 25% water. The signals for samples containing 50% water are much lower than the signals for low-water-content samples in the first 60 min but approach similar intensity of after 60 min. These observations differ slightly from the results of Fromberg et al.²⁷ and Santos et al.26 For example, the IR signals do not increase as the water content is increased for the first 20 min of evaporation/adsorption time. The IR signals do increase as the water content is increased if the evaporation/adsorption time is longer than 20 min. Consider the heating process in these experiments, Compared to Figure 5, the presence of water in the soils can help in releasing the organic compounds out of the soil matrixes effectively as also reported by Fromberg et al.²⁷ and Santos et al.²⁶ In considering the heating efficiency for this type of sampling method, most of the thermal energy is used to vaporize water molecules at first. It will take a longer time to heat the sample to the desired temperature for a high-water-content soil. Therefore, the analytical signals for highwater-content samples are much lower in the first 60 min. On the basis of the above observations, it is clear that analytical signals at any evaporation/adsorption time are less affected if the water content in the range of 10-25%. If there is a large variation of water content in the soil samples, quantitative analytical results can still be obtained by using longer evaporation/adsorption time, i.e., 60 min.

To further study the effect of temperature, three different temperatures of heating were used to evaporate water containing soils. In dry soil samples, the hollow-waveguide sampler can tolerate temperatures as high as 140 $^{\circ}\text{C}$ without obvious change. However, in water-content samples, the heating temperature should be lower than 140 $^{\circ}\text{C}$ because serious distortion of the PIB-coated hollow waveguide sampler was observed for soil samples containing 50% water.

To observe the temperature of the hollow-waveguide sampler at different heating temperatures, a thermal couple was inserted

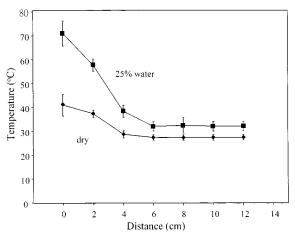


Figure 7. Plot of temperature distribution of hollow waveguide sampler for 25% water content soils and dry soils. Each point was averaged from triplicate runs. One standard deviation was also shown for each point.

into the sampler at varying depths. The temperature after 5 min equilibrium was recorded for dried soil samples or soil containing 25% water. The results are shown in Figure 7. As can be seen in this figure, the temperature at the entrance of the hollow-waveguide sampler for dried-soil samples is around 40 °C but lowers to room temperature in the middle of the hollow-waveguide sampler. For soil containing 25% water, the temperature increases to 70 °C in the entrance of the sampler. In the middle of the sampler, the temperature decreases to 30 °C. This indicates that the energy of the vaporized water molecules transfers to the environment effectively. Although the temperature of the hollow waveguide is lower than 100 °C, no condensation of water molecules inside the hollow-waveguide sampler is observed.

Linearity and Detection Limits for Various Volatility Compounds in Soils. To study the limitations of this method in the analysis of organic species in soils, four compounds of different volatility were used, including 1-CN, CB, 2-CT, and TCE. The literature 38,39 values of the vapor pressures at 25 $^{\circ}\text{C}$ for 1-CN, 2-CT, CB, and TCE are 0.017, 3.55, 12.05, 74.27 Torrs, respectively. The 1-CN is used to indicate less volatile compounds such as polyaromatic hydrocarbons, polycyclic biphenyls, or some chlorinated pesticides (DDT type of compounds). According to literature values, these compounds have lower or similar vapor pressure to 1-CN (0.017 Torr). 2-CT and CB have vapor pressure of 3.55 and 12.05 Torrs, respectively, and these compounds were used to indicate the suitability of this method in the examination of compounds of medium volatility that are commonly examined in soils. TCE (74.27 Torr) was used to demonstrate the limitation of this method in the detection of highly volatile compounds. Using the method developed above, runs for concentration of 25 ppm of the probe molecules and addition of 25% water to the soil samples were performed. Each concentration was run in triplicate. In these experiments, a 5% PIB-coated hollow-waveguide sampler was used. The pneumatic pump was operated at an air flow rate of 5 mL/min, and the heating temperature was kept at 120 °C. Spectra were collected by co-adding 100 scans with 4 cm⁻¹ resolution. The sampling time profiles of IR signals are shown in

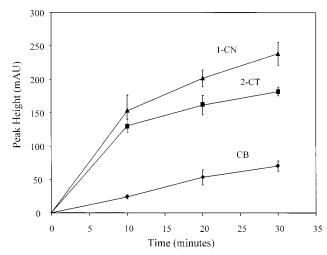


Figure 8. Time profiles for different volatility compounds in soils using a heating temperature of 120 °C. Samples contained 25 ppm of the analytes in soils containing 25% water. Each point was averaged from triplicate runs. One standard deviation was also shown for each point.

Figure 8. As can be seen in these plots, similar sampling time profiles were obtained. The linear regression result of 1-CN at five concentrations (50, 25, 10, 5, and 1 ppm) showed an R-squared coefficient of 0.9993 and its detection limit based three times of signal-to-noise ratio of the lowest concentration signals was 400 ppb. This reveals that, for low-volatility compounds, the developed method is highly suitable. For compounds with medium vapor pressure, the obtained R-squared coefficients were 0.9978 and 0.9993 for 2-CT and CB, respectively. On the basis of the lowest detectable concentration signals, the detection limits for these two compounds were 707 and 905 ppb. These results indicate that compounds with vapor pressure lower than 12 Torr at 25 °C are also detectable but the detection limit is slightly higher. Basically, the efficiency in removal of analyte from the soil matrix increases for higher volatility compounds. However, high-volatility compounds can also more easily escape out of the SPME phase. Because the heating temperature was 120 °C, the efficiency in escaping from the soil should be very similar. Therefore, the vaporization of the trapped analytes was the main cause to determine the applicability of this method for analysis. As the examination results show, a higher detection limit was obtained for more highly volatile compounds such as CB or 2-CT. In attempting to examine highly volatile compounds, such as TCE, IR signals can also be obtained but gas-phase TCE was observed. This reveals that the TCE in the hollow-waveguide sampler was partially vaporized. This limits the application of the sampling method to the examination of highly volatile compounds (higher than 70 Torrs).

CONCLUSION

In this work, a fast and simple method in the detection of chlorinated aromatic compounds in soil samples was proposed. A hollow waveguide was employed with its inner surface coated with hydrophobic film which could adsorb chlorinated compounds vaporized effectively from the soil samples. The speed also increased due to the external heating of the soil

sample. Anoptimal heating temperature was found around 120 °C which reduces the distortion of the hollow waveguide sampler and increased the evaporation efficiency. Moisture in soils can increase the evaporation of the analytes effectively. With 10-min sampling time, high linearity of the standard curves, and low detection limits (around 500 ppb) can be easily achieved for chlorinated compounds with vapor pressures lower than 12 Torrs.

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