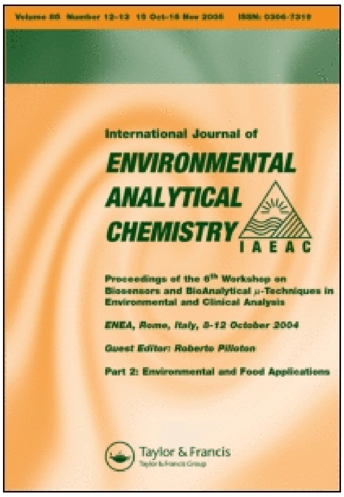

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Combination of Porous Membrane and FT-IR Spectrometry for Detection of Chlorinated Semivolatile Compounds in Soils

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To cite this Article Yang, Jyisy and Chen, Wan-Chan(2001) 'Combination of Porous Membrane and FT-IR Spectrometry for Detection of Chlorinated Semivolatile Compounds in Soils', International Journal of Environmental Analytical Chemistry, 79: 3, 199 — 216
To link to this Article: DOI: 10.1080/03067310108044399
URL: http://dx.doi.org/10.1080/03067310108044399

Intern. J. Environ. Anal. Chem., Vol. 79(3), pp. 199-216
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COMBINATION OF POROUS MEMBRANE AND FT-IR SPECTROMETRY FOR DETECTION OF CHLORINATED SEMIVOLATILE COMPOUNDS IN SOILS

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(Received 22 May 2000; In final form 4 August 2000)

In this paper, a new method is reported for determining semivolatile aromatic compounds in soils. Porous membranes were used as a sampling medium to adsorb analytes that evaporated from soil samples. The adsorbed analytes were examined by Fourier-Transform infrared (FT-IR) spectrometry in the transmittance mode. To accelerate the speed of evaporation, the soil samples were heated to various temperatures, and to increase the adsorption efficiency, porous membranes were further coated with hydrophobic materials. Besides the heating temperature and the properties of the coating materials, several other factors that influence the infrared signals were also examined. These factors include moisture content, sampling time, coating thickness, volatility, and concentration of analyte. Using optimal conditions, the detection limits for semivolatile aromatic compounds can be lower than 100 ng/g.

Keywords: FT-IR; membrane; soils; semivolatile compounds

INTRODUCTION

Organic contaminants in solid samples are usually determined by soxhlet extraction followed by separation and identification. In recent years, methods to reduce the use of organic solvents and to increase the speed of analysis have been proposed. These include supercritical fluids extraction (SFE),[1,2] accelerated solvent extraction (ASE)[3], sub-critical fluid extraction[4,5], and headspace solid-phase microextraction (HS-SPME)[6,7]. Separation and identification methods such as gas chromatography/mass spectrometry are typically used to analyse the extracts. Although sample preparation time can be largely reduced by the dif-

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ferent extraction methods, the analysis time is still limited by the separations. Unlike extraction/chromatographic methods, Fourier-Transform infrared (FT-IR) spectroscopic methods can provide a fast way of examination of environmental samples. However, FT-IR spectrometry cannot be used directly to examine soil samples because the strong spectral interference from the soil matrix. For instance, the silicon or aluminum oxides are the major components in soil, which exhibit strong infrared absorption. To facilitate the analyses of organic contaminants in soils, extraction of the sample is required prior to their identification. More recently, the combination of solid-phase microextraction (SPME)[8–9] with FT-IR spectrometry has provided a convenient way to examine soil samples[10]. In this method, thermal energy was applied to the sample to effectively evaporate the organic compounds out of the soil matrix. The vaporized analytes were directed into a sandwich type of flow cell. The cell was constructed with a hydrophobic film coating the internal reflection elements (IREs). The hydrophobic film on the IREs worked as SPME phase to absorb any vaporized analyte. The absorbed analytes were then examined by the principle of attenuated total reflection (ATR)[11]. Although this method was proved to be highly sensitive in the detection of aromatic compounds in soils, the construction of the ATR sensing cell is tedious and required highly skillful to prevent any rupture of the IREs during the assembling of the cell. Therefore, to eliminate the associate problems in ATR/FT-IR type of detection, we employed a porous membrane coated with suitable polymeric materials to adsorb vaporized analytes. The adsorbed analytes were identified by FT-IR spectrometry using the transmission mode. To quantitatively examine the soil samples, this method was theoretically considered and the details are given in the next section.

METHOD DEVELOPMENT

The basic principle of this method is shown in Figure 1. A membrane is used to adsorb vaporized analytes from the soils. If the analytes adsorb rapidly and remain immobilized in the membrane, 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 present in the membrane should be related to their volatility, the interaction between the soil matrix and the analytes, and the adsorption efficiency of the membrane. Meanwhile, the adsorbed analytes can escape from the membrane because the upper part is in contact with the air. Therefore, three major steps in sampling by this proposed method can be recognized: (1) vaporization of analytes from the soil matrix to the headspace,

(2) adsorption of vaporized analytes from headspace to membrane, (3) the removing of adsorbed analytes from the membrane.

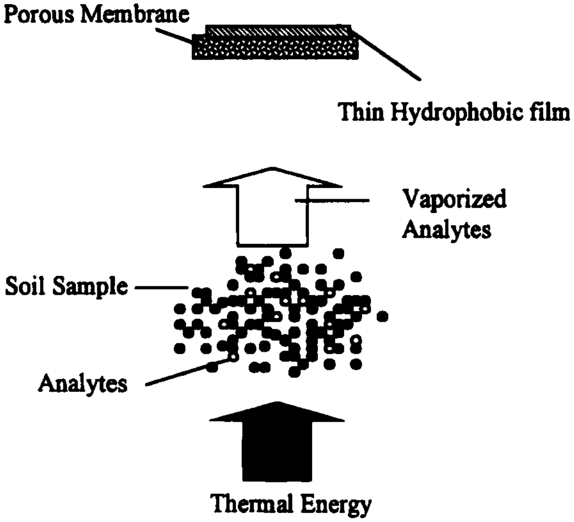

FIGURE 1 Schematic diagram of the principle of porous membrane/IR method proposed

In the first step, both volatility of analytes and 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[12,13]. Basically, the vapor pressure of the analyte strongly affects the efficiency of the evaporation of analyte out of the soils. This vapor pressure 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.

Assuming the heating temperature remained constant, the number of molecules removed from the soil sample at time t can be given by an exponential function:

$$F_l(t) = D_l \times m_l \times [\exp(-h \times t)] \qquad (1)$$

where $F_l(t)$ is a function of the total number of analyte molecules removed at time t, D_l is a proportionality constant, m_l is the amount of analytes in the original soil sample which should be equal to C_0 (original concentration) × weight of soil sample, and h is a constant related to the volatility of the analytes.

In the second step, the vaporized analytes in the headspace can form positive pressure inside the sample vessel. This pressure directs the vapor to pass through the porous membrane. If no other vaporizable compounds in the matrix exist the forming pressure will be very small because the concentrations of analytes are typically lower than 10 μg/g. However, the linear range in this detection method should be relatively small because the large concentration difference, the higher differences in the forming vapor pressure, which can cause different passing linear speed of the analytes through the membrane. Meanwhile, if the pore size of the membrane is large enough, the forming pressure will be very similar for large differences of concentrations. On the other hand, if the volatility of the analyte is low, the forming pressure at any time for different analyte concentrations will also be similar. The properties of the porous membrane are also important in the adsorption of the vaporized analytes. For instance, the partition coefficients of analytes between the membrane and the gas phase strongly affects the adsorption efficiency. To increase this efficiency the surface of the membrane was further coated with hydrophobic materials.

In the third step, the adsorbed analytes in the membrane can also be partially removed because the upper side of the membrane is in contact with air. This desorption process of the analytes can be modeled by the following exponential function:

$$F_2(t_1) = D_2 \times m_2 \times [\exp(-g \times t_1)] \tag{2}$$

Where $F_2(t_1)$ is a function of the adsorbed molecules that have been removed after the elapsed time t_1, D_2 is a proportionality constant, m_2 is the amount of adsorbed analytes that were present at any time t and g is a constant related to the affinity of analytes to the membrane and to their volatility.

By combining equation (1) and equation (2), the amount of analytes present at any time in the membrane can be obtained as follows the integration process is refered in reference 14:

$$F(t) = D_3 \times g \times h \times m_1 \times [\exp(-h \times t) - \exp(-g \times t)]/(g - h) \tag{3}$$

where D_3 equals $D_1 \times D_2$. This equation indicates that analytical signals can be obtained at any sampling time under the same heating temperature. To fit with experimental data, equation (3) is further simplified to equation (4):

$$F(t) = D \times [\exp(-h \times t) - \exp(-g \times t)]/(g - h) \tag{4}$$

where D equals $D_3 \times g \times h \times m_1$.

EXPERIMENTAL

Apparatus

The diagram of the proposed setup is shown in Figure 2. A 7-mL vial with 16.8 mm o.d. was used as extraction chamber, which was placed in a heating oven. A temperature controller was used to control the temperature of the heating zone. An 8-mm diameter hole was drilled on the cap of the sample vial. Membrane was cut into 12 mm in diameter and placed on the cap hole Two Teflon membranes of 0.5-mm thickness were used to seal the sample vessel. After evaporation of the analytes from soils and the adsorption onto the membrane, the cap containing the membrane was moved to the FT-IR spectrometer for recording the infrared spectra.

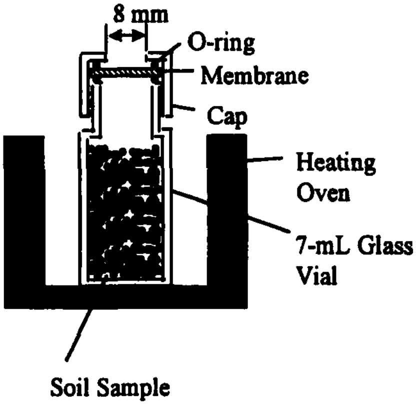

FIGURE 2 Schematic diagram of the set up of porous membrane/IR method used

Materials and Reagents

Polyisobutylene (PIB) was obtained from Aldrich (Milwaukee, USA). Diethyl ether (TEDIA, Fairfield, Ohio) was used to dissolve the probe molecules. Toluene obtained from the same company was used to dissolve the PIB polymer. 1-chloronaphthalene (1-CN), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2-dichlorobenzene (1,2-DCB), 2-chlorotoluene (2-CT), and chlorobenzene (CB) were used as probe molecules for representing different volatility of chlorinated aromatic compounds (Merck, Schuchardt, Germany). The vapor pressures for these probe molecules are 0.017, 0.29, 1, 3.55 and 12.05 Torr for 1-CN, 1,2,4-TCB, 1,2-DCB, 2-CT, and CB, respectively. Because the volatile compounds were defined as vapor pressure larger than 1 Torr, 1-CN, 1,2,4-TCB, and 1,2-DCB were used to represent semi-volatile compounds and 2-CT and CB were used to represent more volatile compounds.

Three types of membranes obtained from Lida Manufacturing Corp. (Kenosha, WI) were examined including polycarbonate (PC) with pore size of 10 µm, polypropylene (PP) with pore size of 0.45 µm, and Teflon with pore size of 0.45 µm.

The soil used as solid matrix was a gift from the Department of Soil Science, National Chung-Hsien University in Taiwan. The obtained soil (Clay loam) contains 24.7% sand, 36.1% slit, and 39.2% clay and used without any pretreatment.

To ensure the cleanness of the soil, IR spectra were acquired before used as solid matrices. No absorption bands were present in the interested spectral region, which will be presented in the results and discussion section. Represented chlorinated compounds were dissolved in diethyl ether to form 2% wt/vol solution. A certain amount of the formed solution was added into 4 g of soil and vigorously shaken in a sealed volumetric flask. The samples were further air dried for 30 minutes to remove the organic solvent.

Procedure of sampling and detection

After the target organic compounds were added to the soil samples to the desired concentrations of analytes, soil samples were placed into the sample vial. The sample vial was placed into the heating oven. A Fourier transform infrared spectrometer (Magna 550, Nicolet) equipped with Mercury Cadmium Telluride (MCT) detector was used to detect the absorbed analytes.

Typical transmittance spectra of the examined membranes are shown in Figure 3. Each spectrum was obtained by accumulating 100 scans at 4 cm^{-1} resolution. As can be seen in this figure, the transmittance of PC is better than that of Teflon or PP, but it exhibits several strong and broad absorption bands in the region lower than 1000 cm^{-1}. Meanwhile, the transmittance of Teflon was much lower than any other membranes. Therefore, PP membrane was used as substrate for adsorption of probe molecules.

To increase the adsorption capability, the surface of PP membrane was coated with PIB. The transmittance spectrum of the PIB coated PP membrane was also shown in Figure 3. As can be seen in the spectrum, the coated membrane 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, and makes it especially useful for the detection of halogenated compounds. Two small peaks of PIB located at 950 and 923 cm^{-1} were used as an indication of the film thickness of the PIB coating.

Typica spectra of the probe molecules measured by this method were shown in Figure 4. Two strong absorption peaks located around 700 cm^{-1} can be found in the spectrum of 1-CN and the peak located 766 cm^{-1} was selected as an indication of the amount of 1-CN being detected. For the rest of compounds, the used peaks were indicated by an arrow in Figure 4. The membrane can be easily regenerated by simply placing it into hood and evaporate for a certain period of

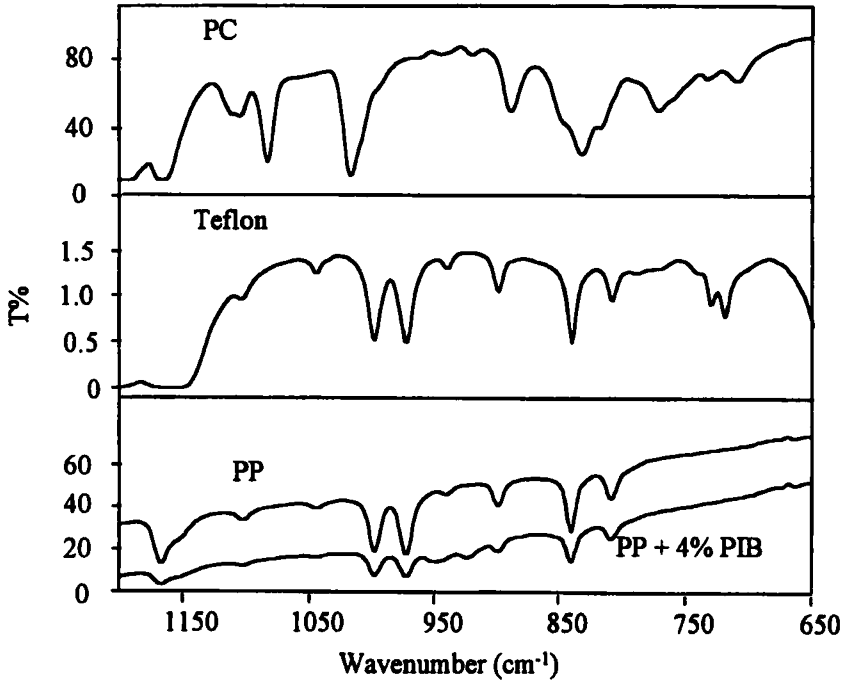

FIGURE 3 Transmittance spectra of polycarbonate (PC), Teflon, and polypropylene (PP) porous membranes

time (typically 2 hours). By this procedure, no IR signal from the probe molecules was observed. Meanwhile, no significant change of the PIB absorption band intensity was observed after regeneration of the membrane. Because the production of the PIB coated membranes are so simple, new membranes were used in this work.

RESULTS AND DISCUSSIONS

Time profiles of IR signals

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

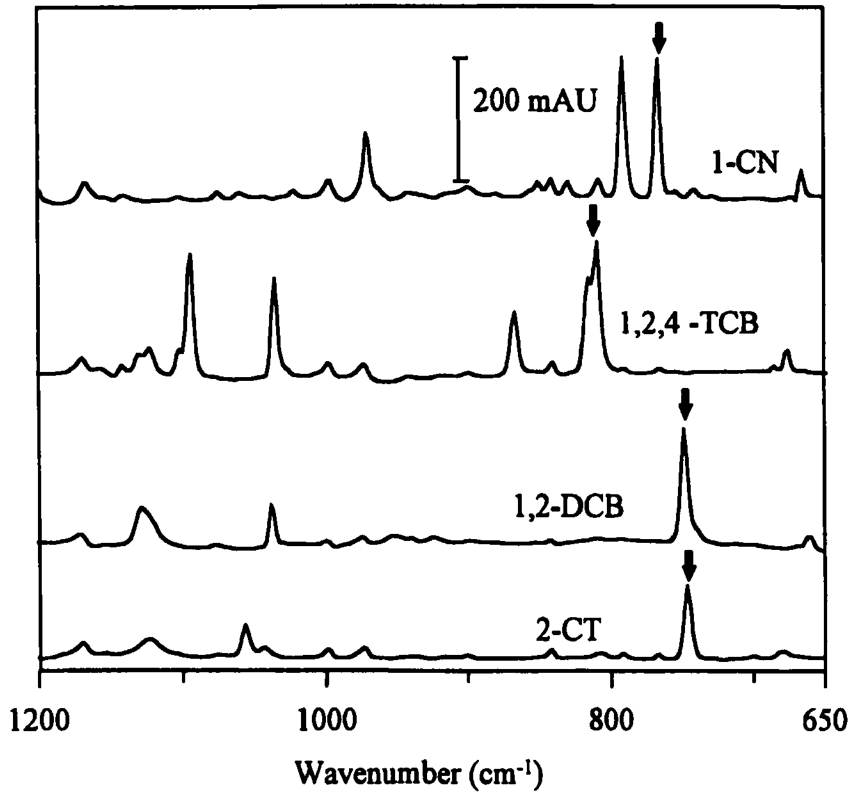

FIGURE 4 Typical IR spectra of 50 μg/g of 1-chloronaphthalene (1-CN), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2-dichlorobenzene (1,2-DCB), and 2-chlorotoluene (2-CT)

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 the adsorption efficiency, 10 μL of the 2% 1-CN solution (200 μg of 1-CN) were placed into the sample vial. After air-dried, the sample was heated up to 130°C and a PP membrane was used to adsorb the analyte. Results are shown in Figure 5. As can be seen in this figure, the 1-CN signals increased as the adsorption time increased. When membrane was coated with 6% PIB, the 1-CN signals were largely increased. This indicates that the adsorption efficiency was largely increased if PIB was placed on the top of the membrane. A high agreement between equation (4) and experimental data has also been observed (Figure 5).

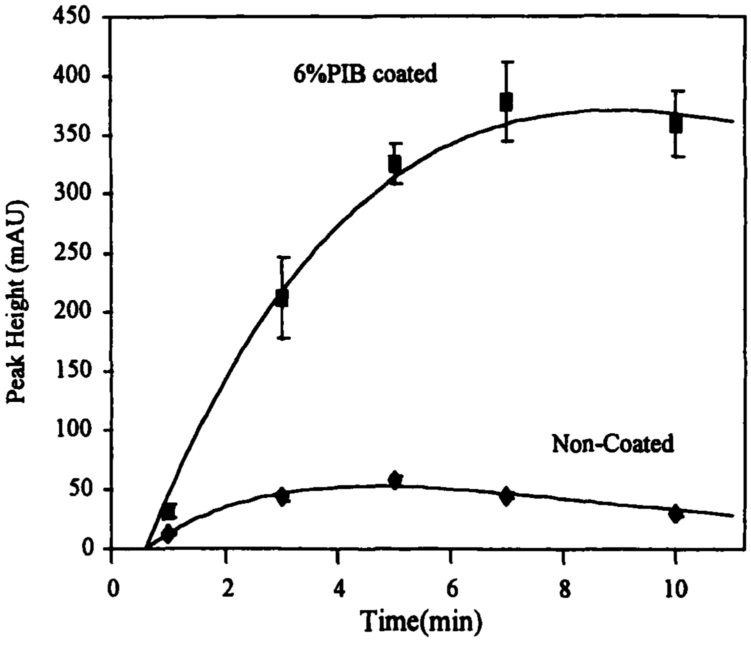

FIGURE 5 Extraction/Adsorption time profiles for detection of 200 μg of 1-CN by PP(◆) and 6%PIB coated PP(■) One standard deviation based on triplicate runs was also plotted as shown by error bar. The extraction temperature was 130°C

Because 1-CN exhibits a vapor pressure of 0.017 Torr, it was expected to desorb from the membrane. Therefore, the removing efficiencies for PP and PIB coated PP membranes were examined and the results are shown in Figure 6. In this plot, the 1-CN adsorbed membrane was placed in the hood for the examined time. The signals decreased exponentially but the retaining of the analyte in the membrane was much higher for the 6% PIB coated membrane. By fitting experimental data with equation (2), the results indicated that equation (2) can be used to model the desorption behavior of the adsorbed analytes.

Effect of thickness of PIB coating on the membrane

Different concentrations of PIB solutions were used to coat the PP membrane. The reproducibility and linearity of the coating procedure are shown in Figure 7. As can be seen in this figure, the PIB signals (integrated peak area of peaks located at 950 and 923 cm^{-1}) increased as the concentration of the PIB increased.

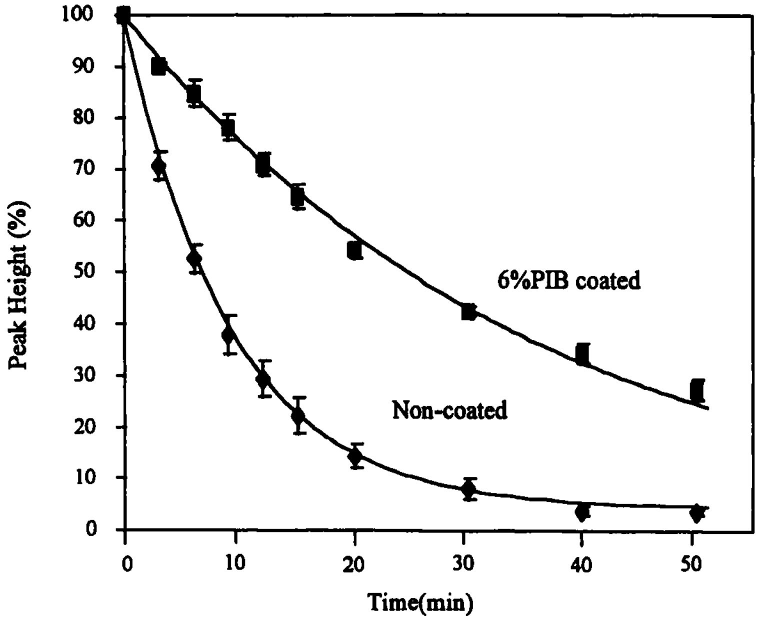

FIGURE 6 The retaining efficiencies of PP (♦) and 6%PIB coated PP(■). Plot of 50 μg/g 1-CN signals at different heating temperature

This reveals that the concentration of the PIB solution can be used to control the thickness of PIB. The standard deviation, calculated on the basis of triplicate runs, is also shown in this plot. As can be seen, the reproducibility in any of the PIB concentrations was lower than 5%.

To examine the effect of the PIB thickness on adsorption, the 10 μL of 1-CN (200 μg 1-CN) solution was placed onto the sample vial. After air-drying, PIB coated membranes were used to adsorb the vaporized 1-CN (heated to 130°C). The obtained IR signals for 7 minutes evaporation/adsorption times were plotted in Figure 8. As can be seen in this figure, the IR signals increased as the thickness of PIB increased and the increasing rate of the IR signals was slower beyond 4% PIB coating However, when high concentrations of PIB solution were placed on the membrane, the transmittance of IR radiation was also reduced. Therefore, the noise level increased as thickness of PIB increased. The peak-to-peak noise level for a 2% PIB coating was around 0.144 mAU but around 0.190 mAU for a 8% PIB coating. Therefore, in the following experiments, the 4% PIB solution was used to coat the membrane.

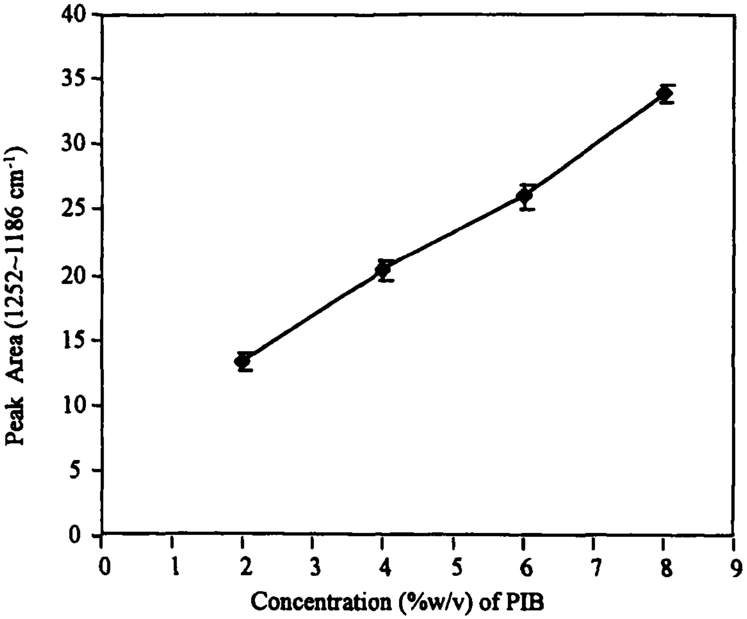

FIGURE 7 Relationships between film thickness of PIB and the concentration of PIB solutions. 90 μL of PIB solution was placed on the surface of PP. After air-dried, IR spectra were measured and the intensities of PIB peaks located around 950 and 923 cm^{-1} were integrated as the indication of PIB thickness

Effect of moisture

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 different soil water contents The forming water pressure can affect the flow rate of the vaporized organic compounds through the membranes. Meanwhile, the vaporized water molecules can be condensed on the surface of the membrane to block the adsorption surface of the membrane. To study the effect of soil matrix and water, 10 μL of 1-CN solution was placed into 4 g of soil to form a 50 μg/g of soil sample. This sample was added with and without 0.4 mL of water. By keeping the heating temperature of the samples at 130°C, the obtained IR signals plotted with evaporation/adsorption times are shown in Figure 9. The curve for 1-CN without soil matrix was also plotted in this figure. As can be seen, the soil matrix strongly interacts with analytes as that the obtained IR signals were much smaller for dry soil than that of no soil matrix. When water was added into the soil, very similar

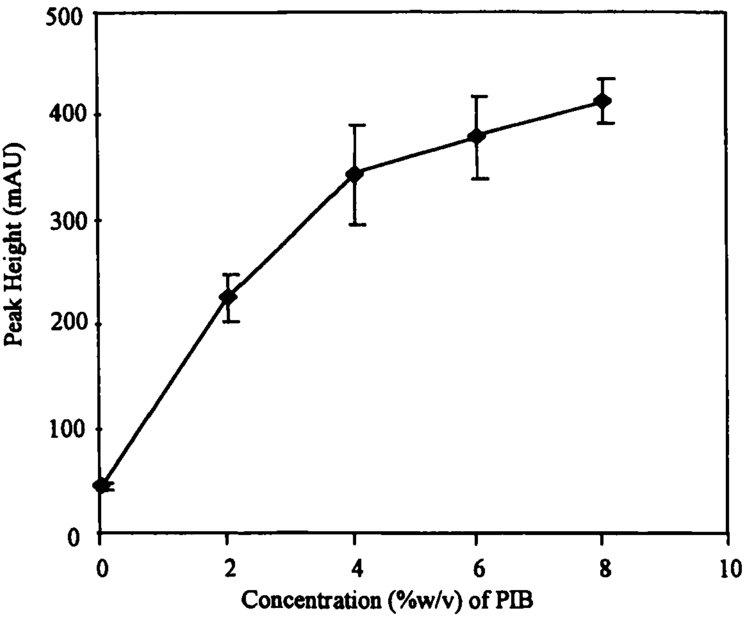

FIGURE 8 IR signals of 1-CN obtained using PP membranes coated with different concentration of PIB. The extraction/adsorption time was 7 minutes for detection 200 μg of 1-CN (heated to 130°C)

intensities of IR signals were obtained. This indicates that water can release the organic analytes out of the soil.

In this specific experiment, the heating temperature was above the boiling point of water and the time to finish the analysis was shorter than 10 minutes. To further study the effect of moisture, heating temperatures of 70 and 90°C were used. Soil samples containing 50 μg/g of 1-CN were examined by addition of 0.4, 0.8, 1.2, 1.6 and 2.0 mL of water. Results are shown in Figure 10. As can be seen, the IR signals increased gradually, much slower and less intense than in 130°C. For example, the maximum signal appeared at 7 minutes for 130 °C. For 70°C, the maximum signal was located around 30 minutes although of much lower intensity. This is understandable because the low temperature in heating reduces the vaporization of the analytes. According to the results of Santos *et al.*[15], the extraction efficiencies for three chlorobenzenes in soils were increased if a large amount of water was added to the soils. However, in our experiments, the signals of the analytes were more intense in low water contents. For instance, the IR signals at 70 or 90°C for samples containing 0.4 and 0.8 mL of water were higher than that of samples with 1.2 mL of water. To examine the

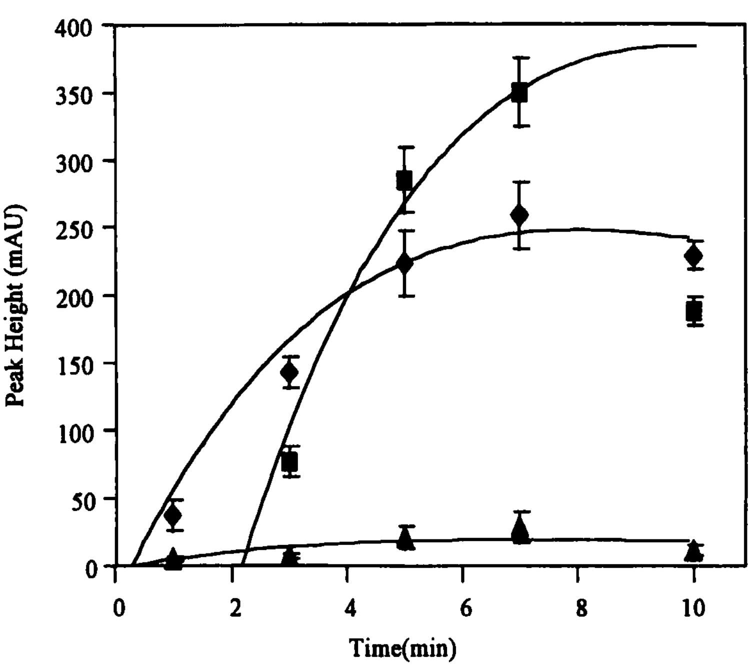

FIGURE 9 Effect of matrix on determination of 200 μg of 1-CN. These samples include without soil (◆), with 4 g of soil (■) and 4 g of soil containg 0.4 mL of water (▲). Samples were heated to 130°C. Standard deviations based on triplicate runs were also plotted

effect of water contents, the IR signals were obtained after 15 minutes and at a heating temperature of 90°C.

As can be seen in Figure 11, the IR signals increased to a certain level after which a decrease occurred. This may reveal that the addition of water can effectively release the adsorbed analytes in the soil matrix, especially when the amount of water was lower than 0.8 mL. Decreases of the IR signals were observed after the amount of water was larger than 1.0 mL. This indicates that the heating efficiency decreased by the addition of large amounts of water to the sample.

Effect of temperature for different compound volatilities

To study the limitations of this method in analysis of organic species in soils, five different compounds were used, including 1-CN, 1,2,4-TCB, 1,2-DCB, 2-CT, and CB. The vapor pressures for these target compounds are 0.017, 0.29, 1.0,

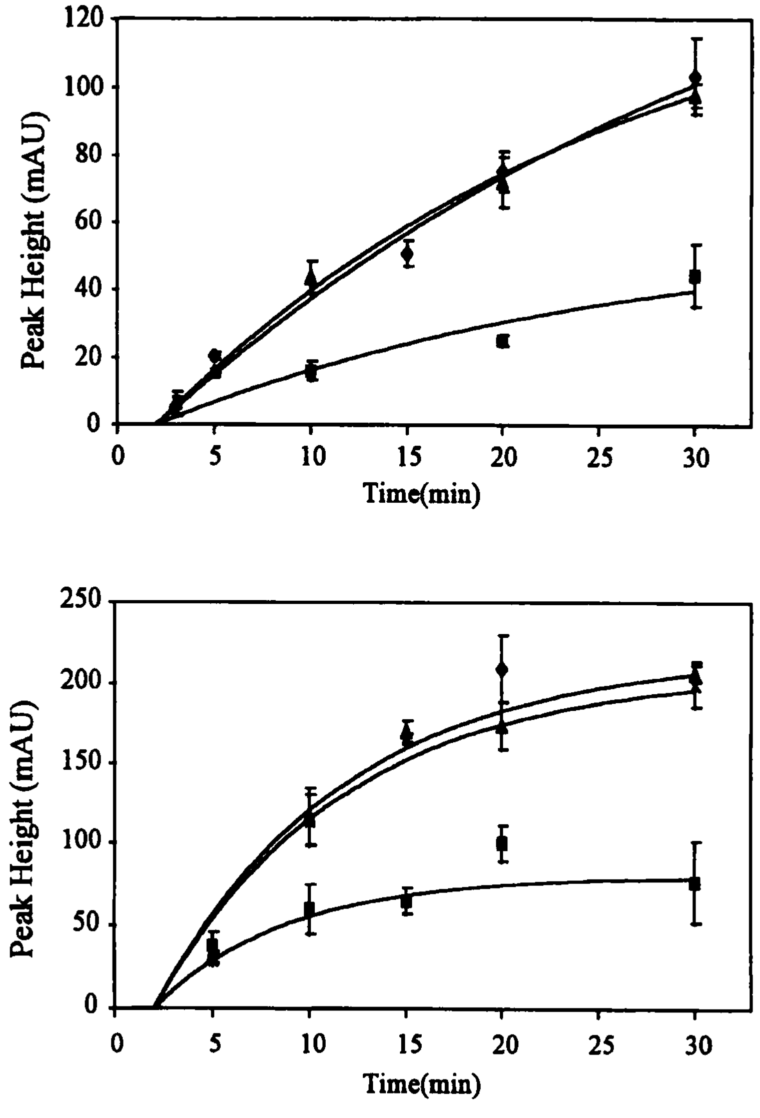

FIGURE 10 Extraction/adsorption time profiles for three different water content samples. 50 μg/g 1-CN in 4 g of soil was added with 0.4 (▲), 0.8 (■) and 1.2 mL(◆) of water. Two heating temperatures were studied including 70°C (A) and 90°C (B)

3.55 and 12.05 Torr for 1-CN, 1,2,4-TCB, 1,2-DCB, 2-CT, and CB, respectively. The 1-CN was used to indicate less volatile compounds such as polyaromatic hydrocarbons, polycyclic biphenyls or some chlorinated pesticides (DDT type of

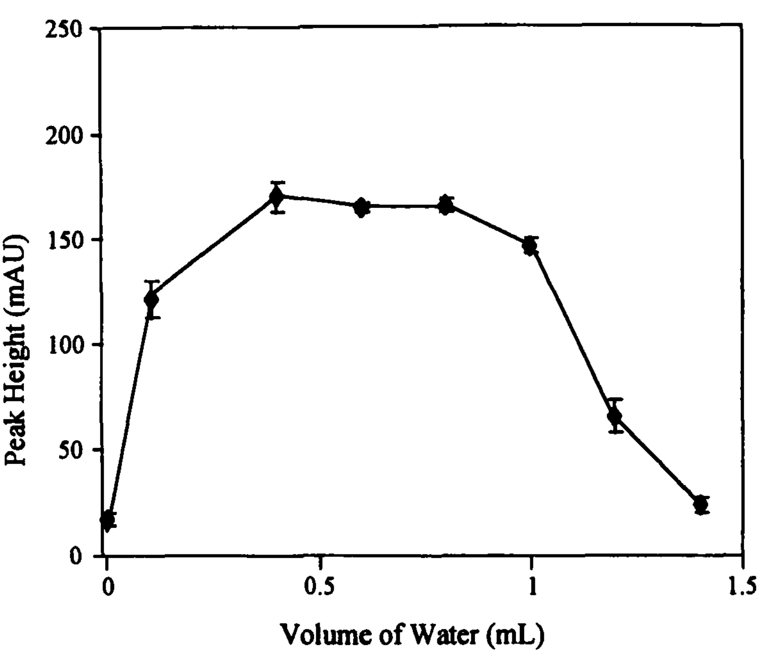

FIGURE 11 Effect of moisture on extraction/adsorption of 50 μg/g 1-CN in 4 g of soil. Different volumes of water were added into the soil. Heating temperatures was 90 °C for these tuns

compounds). According to literature values, these compounds have lower or similar vapor pressure to 1-CN (0.017 Torr). The 1,2,4-TCB, 1,2-DCB, 2-CT, and CB were used to indicate the suitability of this method in the examination of medium to high volatility compounds that are commonly analysed in soils. Using the method developed above, runs for concentrations of 50 μg/g of the probe molecules and addition of 0.4 mL of 0.4 mL of water to the soil samples were performed. Each concentration was run in triplicate. In these experiments, a 4% PIB-coated PP membrane was used. Figure 12 shows the IR signals obtained after 10 minutes evaporation/adsorption time. As can be seen in this plot, the optimal temperature was varied for different volatility compounds. For example, the IR signals increased as the heating temperature increased. For 1,2-DCB and 1,2,4-TCB, maximum IR signals were obtained between 50 to 100°C. For high volatility compounds such as 2-CT, the lower temperature can give higher signals in the examined temperature region. For highly volatile compounds such as CB, this method was restricted because of week obtained signals. In consideration of the influence of water, temperatures lower than boiling point of water were preferred to reduce the chances of water condensation in the surface of membrane. Therefore, in analysis of semivolatile compounds in soil, the heating temperature is suggested between 50 and 100°C.

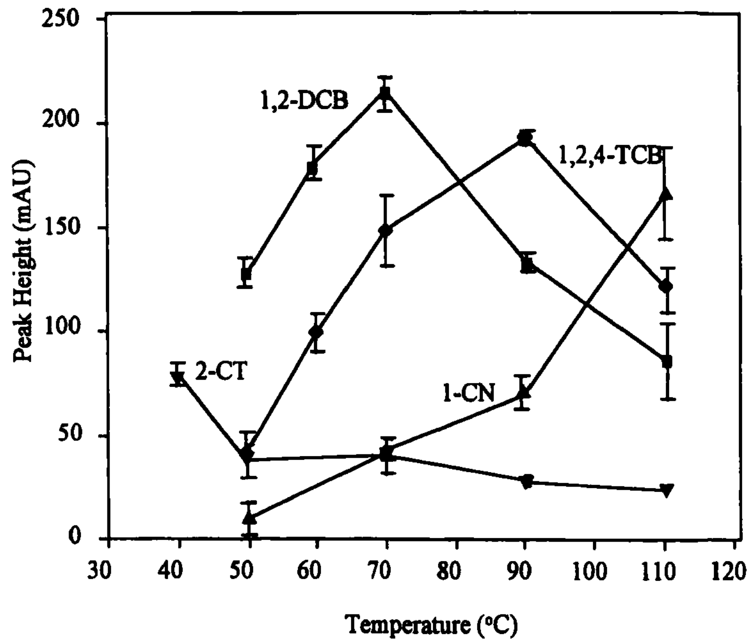

FIGURE 12 Effect of temperature on extraction/adsorption of analyte in 50 μg/g. Spectra were recorded after 10 minutes evaporation time. Four compounds were investigated including 1-CN (▲), 1,2,4-TCB (♦), 1,2-DCB (■) and 2-CT (▼). 0.4 mL of water was also added into the soil

Linearity and detection limits for various volatility compounds in soils

To examine the linearity between IR signals and their concentrations, 0.4 mL of water content samples with different concentrations of 1-CN were first examined and the results are listed in Table I. The results indicate that the linear regression of 1-CN at six concentrations (50, 25, 12.5, 6.5, 3, and 1 μg/g) showed an R-squared coefficient of 0.992 and its detection limit based on three times of signal-to-noise ratio of the lowest concentration signals was 75 ng/g. 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 0.990 to 0.993 for 1,2,4-TCB, 1,2-DCB, and 2-CT. Based on the lowest detectable concentration signals, the detection limits for these compounds were ranged from 80 to 143 ng/g. These results indicate that for compounds with vapor pressures lower than 3.55 Torr at 25°C are also highly suitable. In analyses of highly volatile compounds, such as CB, the detected signals were weak and the linear relationship between IR signals and concentration was poor. Therefore, this method was restricted to compounds that have vapor pressures higher than 12 Torr, whereas for compounds having vapor pressure between 3.55 to 12 Torr the results are questionable.

TABLE I Obtained analytical results for probe molecules

Compounds	*Vapor Pressure (Torr)*[a]	*IR signals (mAU)*[b]	*DL*[c] *(ng/g)*	*R-Square*[d]
1-CN	0.017	227.6(±7.4)	51	0.992
1,2,4-TCB	0.29	214.9(±4.4)	64	0.994
1,2-DCB	1.00	184.6(±3.5)	89	0.990
2-CT	3.55	119.9(±13.5)	151	0.993
CB	12.05	8.0(±3.4)	2138	--

a. Adapted from references 12 and 13.

b. 50 μg/g of chlorinated aromatic amines were examined in 4 cm^{-1} resolution and coadded in 100 scans. Evaporation/adsorption time for 1-CN and 2-CT was 15 minutes and 10 minutes for rest of the compounds. Heating temperatures were 90, 90, 70, 40 and 40°C for 1-CN, 1,2,4-TCH, 1,2-DCB, 2-CT and CH, respectively.

c. Detection limits were calculated based on the ratio of IR signals at 1 μg/g and three times of peak-to-peak noise. CB was calculated based on the signals of concentration at 50 μg/g.

d. The examined concentration was in the range of 1 to 50 μg/g.

CONCLUSION

In this work, a fast and simple method for the detection of chlorinated aromatic compounds in soil samples was proposed. The employed coated porous membrane can adsorb chlorinated compounds vaporized from the soil samples. Optimal heating temperature was found to be lower than 90°C to reduce the distortion of the membrane and to increase the evaporation efficiency. Moisture in soils can increase the evaporation of the analytes effectively. With 10 minutes sampling time, high linearity of the standard curves and low detection limits (around 100ng/g) can be easily achieved for chlorinated compounds with vapor pressures lower than 3.55 Torrs.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China for financially supporting this work under the Contract No. NSC88–2113-M-033–008.

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