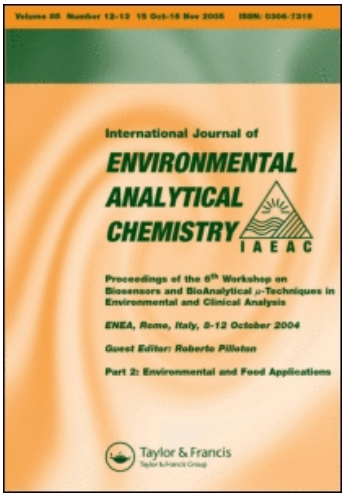

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Reflection-absorption infrared sensing device for detection of semivolatile aromatic compounds in soils

Jyisy Yang[a]; Wan-Chan Chen[b]
[a] Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan 402 [b] Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan 320

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REFLECTION–ABSORPTION INFRARED SENSING DEVICE FOR DETECTION OF SEMIVOLATILE AROMATIC COMPOUNDS IN SOILS

JYISY YANG[a,*] and WAN-CHAN CHEN[b]

[a]*Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan 402;*
[b]*Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan 320*

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In this article, a new IR-sensing device is described for the examination of chlorinated aromatic compounds in soils. To prepare this sensing device, a 20-mL glass vial was modified for use in the analysis of soil samples by conventional Fourier-transform infrared (FT-IR) spectroscopy. In this sampling device, an aluminium plate coated with a hydrophobic film was placed on top of the cap of the sample vial to absorb the analytes that evaporated from the soil matrix. After this absorption process was complete, the cap was placed in an FT-IR spectrometer, and the absorbed analytes were detected in the reflection–absorption (RA) mode. To accelerate the rate of evaporation of the analytes, the soil samples were heated to various temperatures. Meanwhile, other factors, such as the moisture content, sampling time, thickness of the hydrophobic film, and the volatilities and concentrations of the analytes, were also examined to optimize the analytical conditions. The results indicated that the time required to reach equilibrium conditions was short, and evaporation/absorption could be achieved within 10 min. With a water content of 10% (v/w) or less, the intensities of the analytical signals were increased greatly when compared with those of dry samples; when the water content was above 10% (v/w), these intensities decreased, partially as a result of the heating efficiency. After examining the compounds that had different vapour pressures, the analytical results indicated that this method was applicable to the examination of compounds that had vapour pressures below 1.0 Torr. Using the optimal conditions determined in this study, the detection limits for semivolatile aromatic compounds were lower than 100 ng/g, and the regression coefficients of the standard curves for compounds that had a vapour pressure lower than 1.0 Torr were larger than 0.99 in the concentration range of 1–100 μg/g.

Keywords: FT-IR; Aromatic compounds; Soil sample; Reflection–absorption

INTRODUCTION

Chlorinated aromatic compounds are contaminants commonly found in environmental soil samples. For example, chlorobenzenes and polychlorinated biphenyls (PCBs) are listed as priority pollutants and can be found in a number of matrices [1–5]. Analysis of these compounds in solid matrices, such as soils and sediments, requires several steps for the extraction and preconcentration of the analytes when conventional

*Corresponding author. Fax: +886-422862547. E-mail: jyisy@dragon.nchu.edu.tw

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methods are used, e.g. Soxhlet extraction. Several other extraction methods, such as supercritical fluid extraction [6,7], accelerated solvent extraction [8], and sub-critical fluid extraction [9,10], have been proposed to reduce the amount of organic solvents used and to increase the speed of the analysis of soil samples. The solid-phase microextraction (SPME) method has also been proposed as a means to simplify the extraction and preconcentration steps [11–13]. Headspace solid-phase microextraction (HSSPME) [14–17] was developed recently to extend the SPME method to soil samples. HSSPME is a simple and convenient technique for the sampling of analytes in different sample matrices [14,18–22]. For example, this technique has been used to sample volatile contaminants in food [21] and contaminants in water [14,20] and soils [22]. There are several advantages that result when using the HSSPME method, including shorter extraction times, and it may be applied to any type of matrix [13,14]. Although HSSPME does reduce the sample preparation time, the rate at which the analytes can be determined is still limited by the time required for the separation step to be completed chromatographically.

Unlike chromatographic methods, spectroscopic methods provide fast and simple means for the detection of environmental samples and allow large numbers of samples to be screened in a very short time. Amount them, the Fourier-transform infrared (FT-IR) spectroscopic method not only provides an advantage in terms of speed but also provides information on the structure of the analytes. However, the major applications of FT-IR spectroscopy have been limited mainly to aqueous samples [23–33], and only a few reports have emphasized the detection of analytes from soils [34,35]. This situation has resulted because a soil matrix contains a large amount of strong IR absorbers, including moisture and silicon oxides. To eliminate the interference from these components during analyses, it is typical to apply thermal energy to the soil matrix to evaporate the analytes from the matrix and to concentrate them by the use of a suitable hydrophobic film prior to their analysis.

To simplify the IR spectroscopic method for the analysis of soil samples, in this article a new sensing device is proposed. In this method, a regular 20-mL sample vial was used to sample the analytes. A reflection plate coated with a hydrophobic film was placed on top of the cap. The soil sample was heated to increase the rate of evaporation of the analytes to the headspace of the sample vial where they became absorbed by the hydrophobic film on the cap. After sampling, this cap was placed in an FT-IR spectrometer for detection. The principle of this sampling approach is similar to that of HSSPME because the sampling cap is placed on the headspace. Therefore, the working functions of HSSPME have been adapted in this study, but only a brief description of the process is provided herein.

In conventional HSSPME sampling, organic compounds that have a high affinity toward the hydrophobic film become concentrated in the film, and this extraction process results in a higher sensitivity than that achieved in a conventional headspace analysis [36–38]. Once the partition equilibrium is attained, the amount of extracted analyte can be expressed by the following equation [13,14]:

$$n^{\infty} = (K_{\mathrm{fh}} \times K_{\mathrm{hs}} \times V_{\mathrm{f}} \times V_{\mathrm{s}} \times C_{\mathrm{o}})/(K_{\mathrm{fh}} \times K_{\mathrm{hs}} \times V_{\mathrm{f}} + K_{\mathrm{hs}} \times V_{\mathrm{h}} + V_{\mathrm{s}}), \qquad (1)$$

where K_{fh} is the equilibrium partition constant for the analyte between the headspace and the hydrophobic film, and K_{hs} is equilibrium partition constant for the analyte

between the sample and its headspace. The terms V_f, V_h, and V_s represent the volumes of the SPME polymer film, the headspace, and the sample matrix, respectively. The term C_o reflects the initial concentration of the analyte in the sample matrix. Under conditions in which all the other parameters remain constant, the number of molecules of analyte is proportional to the original sample concentration. Normally, the HSSPME is operated under equilibrium conditions, but the time required to reach the absorption equilibrium between the sample and the hydrophobic film can be very long. In this situation, it is desirable to shorten the absorption time and work under non-equilibrium conditions, even though such an approach is followed at the expense of sensitivity. The dynamic HSSPME model derived by Ai [39–41] indicated that even under non-equilibrium conditions, quantitative results still could be obtained. The working equation developed by Ai indicated that the amount of analyte extracted by the hydrophobic film at absorption time t could be monitored by an exponential function:

$$n^{\infty} = (K_{fh} \times K_{hs} \times V_f \times V_s \times C_o)/(K_{fh} \times K_{hs} \times V_f + K_{hs} \times V_h + V_s), \qquad (2)$$

where n^{∞} is the number of molecules absorbed into the hydrophobic film under equilibrium conditions, and a_h is a complicated parameter that determines how fast the equilibrium can be reached. According to the principle of HSSPME, the influencing factors include the volumes of the sample and the headspace, the heating temperature, and the volatility of the organic compounds. Therefore, these factors were all examined in this study.

EXPERIMENTAL

Apparatus

Figure 1 shows the setup used in this study. A 20-mL vial, which had an o.d. of 27 mm and a height of 53 mm, was used as the extraction chamber and was placed in a heating oven. Five holes, 30 mm in diameter, were drilled on the top of the cover of the oven. A temperature controller was used to control the temperature of the heating zone. Polished aluminium plates were cut into 18-mm-diameter discs and placed on top of the cap of each sample vial. These plates had been coated with hydrophobic materials by the addition of a certain amount of polymer solution and then air-dried for at least 3 h. Two Teflon membranes of 0.5-mm thickness were used to seal the sample vessel. One was cut into an 18-mm-diameter disc and was placed between the cap and the aluminium plate. The other membrane was cut into an 18-mm diameter disc that had a hole of 14-mm diameter in its centre and was placed on the top of the aluminium plate. After assembly, the cap could be sealed tightly. After the soil samples had been placed into this sample vial, the analytes were evaporated from the soil samples and were absorbed into the hydrophobic film on the aluminium plate. When the absorption process was complete, the entire cap was placed into an FT-IR spectrometer, and the infrared spectra were measured in the single reflection–absorption mode. The optical arrangement for this reflection–absorption mode used two mirrors to direct the IR radiation to the aluminium reflection plate and to redirect the IR radiation back to the spectrometer. The image at the bottom of Fig. 1 displays a schematic diagram of

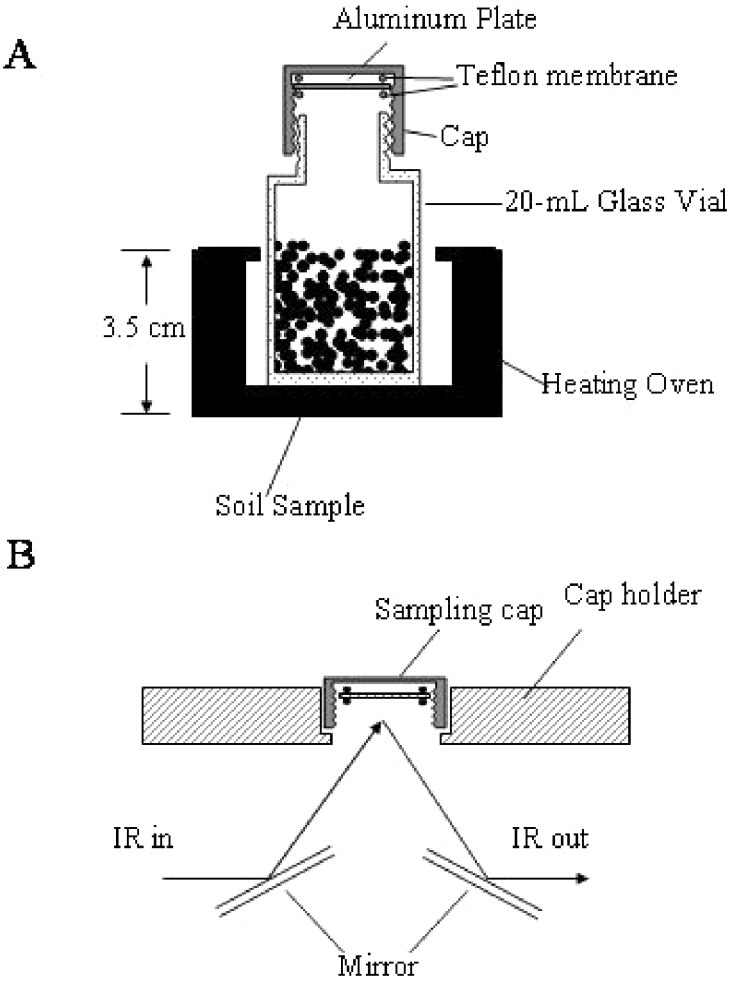

FIGURE 1 (A) Schematic diagram of the sampling device used for the reflection–absorption IR sensing method proposed in this article. (B) Optical arrangement for the detection of the absorption analytes by FT-IR spectroscopy.

this setup. The angle of the incident radiation was around 45° with respect to the normal plane.

Materials and Reagents

Polyisobutylene (PIB) obtained from Aldrich (Milwaukee, WI) was used as the hydrophobic material. Diethyl ether (TEDIA, Fairfield, OH) was used to dissolve the probe molecules. Toluene, which was obtained from the same company, was used to dissolve the PIB. 1-Chloronaphthalene (CN), chlorobenzene (CB), 1,2-dichlorobenzene (DCB), 1,2,4-trichlorobenzene (TCB), 1,2,4,5-tetrachlorobenzene (TeCB), and 1,2,3,4,5-pentachlorobenzene (PCB), which were all obtained from Merck (Schuchardt, Germany), were used as probe molecules that represent the different volatilities of chlorinated aromatic compounds. The vapour pressures of CN, PCB, TeCB, TCB,

DCB, and CB are 0.017, 0.059, 0.067, 0.29, 1.0, and 12.05 Torr, respectively [42–44]. CB exhibits a high volatility and was used to indicate the suitability of this method for the detection of volatile chlorinated aromatic compounds. The soil (clay loam), which was provided as a gift from the Department of Soil Science of the National Chung-Hsing University in Taiwan, contained 24.7% sand, 36.1% silt, and 39.2% clay, and was used without any pretreatment. To ensure that the soil was clean, IR spectra were acquired by the method proposed herein prior to its use as a solid matrix; no absorption bands were observed in the spectral region of interest. The representative chlorinated compounds were dissolved in diethyl ether to form a 2% wt/vol solution. A certain amount of the prepared solution was spiked into 6 g of soil, which was then shaken vigorously in the sample vials. These soil samples were air-dried for a further 15 min to remove the remaining organic solvent.

Procedure of Sampling and Detection

Once the probe organic compounds had been added to the soil samples to form the desired concentrations of analytes, the soil samples were placed into the sample vial, which was then placed into the heating oven. An FT-IR spectrometer (Jasco 420, Tokyo) equipped with a mercury cadmium telluride (MCT) detector was used to detect the absorbed analytes. Typical spectra of the probe molecules measured by this method are presented in Fig. 2. Two strong absorption peaks located at around $700\,cm^{-1}$ could be observed in the spectrum of 1-CN; the peak located at $766\,cm^{-1}$ was selected to provide an indication of the amount of 1-CN being detected. For the remaining compounds, the peaks selected for quantitative analyses are indicated by arrows in Fig. 2. According to the spectra displayed in Fig. 2, the examined compounds are highly amenable to simultaneous analysis because only a few of the absorption bands interfered with one another. Chemomatrix techniques could also be applied to extract quantitative data from the overall spectrum.

Because chlorinated aromatic compounds exhibit high vapour pressures, they were expected to desorb from the sampling cap. Therefore, the trapping efficiencies for these compounds were first examined, and the results are presented in Fig. 3. In this plot, the CN-adsorbed cap was placed in the hood for a period of time. The signals decreased exponentially, and the rate of desorption of each compound was dependent upon its volatility. Basically, the higher the vapour pressure, the faster the desorption from the trapping phases. In terms of quantification, these plots indicated that the lapping time between the absorption and examination should be kept constant. For example, if the cap was examined each time immediately after adsorption, the amount of analytes that desorbed from the cap should be similar. Based on the trapping efficiency, regeneration of the absorption cap becomes possible. Because the method used for the production of the sampling cap was so simple, no attempt was made to regenerate the sensing cap; instead, newly prepared caps were used.

RESULTS AND DISCUSSION

The success of sampling the analytes in the headspace is strongly related to the efficiency of the evaporation of the analytes from the soil matrix. The evaporation efficiency is related to the strength of the interaction between the analytes and the

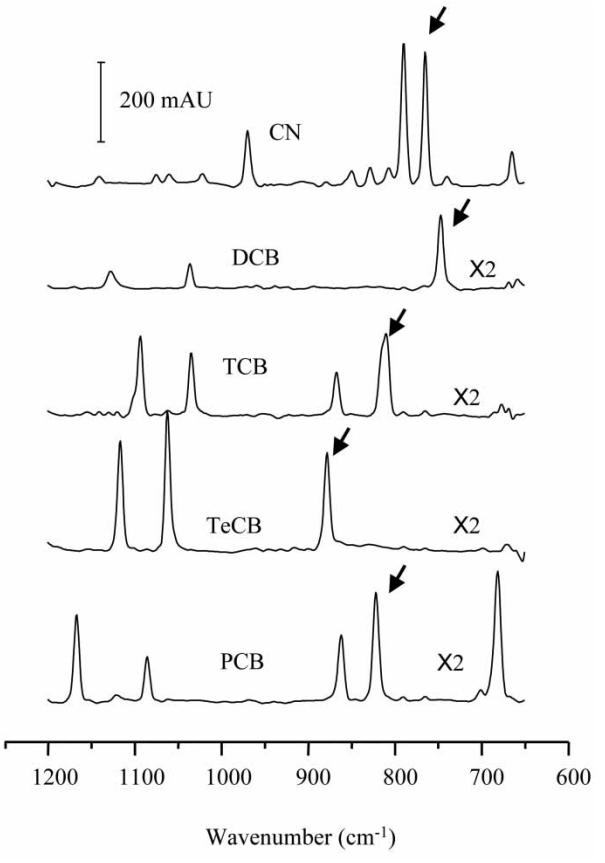

FIGURE 2 Typical IR spectra of 50 μg/g samples of CN, DCB, TCB, TeCB, and PCB. Spectra were obtained by the coaddition of 100 scans at a resolution of 4 cm^{-1}.

soil matrix and to the volatility of the analytes. To overcome the interaction between the analytes and the soil matrix, a releasing agent can be added, and thermal energy can be used to improve the evaporation efficiency. A releasing agent can interact with the active sites in the soil and, hence, release the analytes from the soil matrix. The use of thermal energy can overcome the interaction between the analytes and the soil matrix, and also increase the evaporation efficiency of the analyte. Therefore, the effects of moisture and thermal energy were both studied. Meanwhile, the relationship between the intensity of the IR signals and the volatility of a compound was also examined.

Optimization of the Thickness of the Hydrophobic Film

To determine the thickness of the hydrophobic film on the aluminium plate required for optimal analyses, solutions of PIB were prepared that had concentrations in the range of 2–8% (w/v). After the addition of 90 μL of PIB solution to the aluminium plate and then air-drying, the coated aluminium plates were used to absorb the analyte from 50 μg/g of CN in 6 g of soil that contained 10% (v/w) of water. The peak intensity of CN obtained after sampling for 15 min was plotted against the concentration of

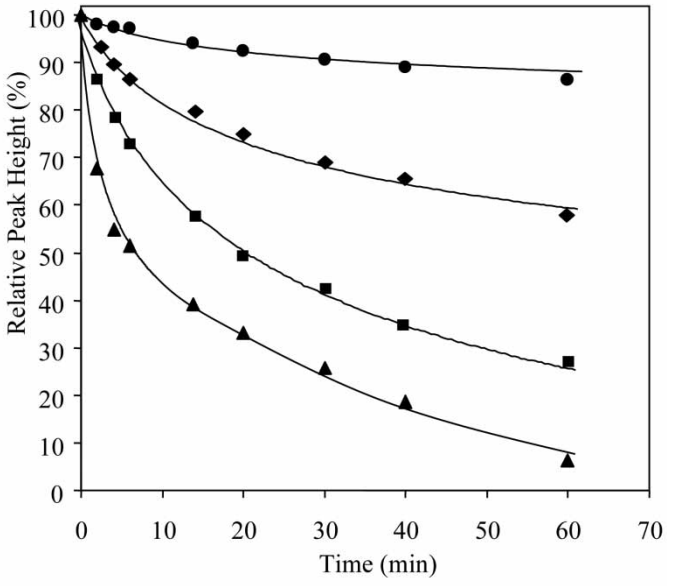

FIGURE 3 Desorption time profiles for PCB (●), CN (■), TCB (◆), and DCB (▲).

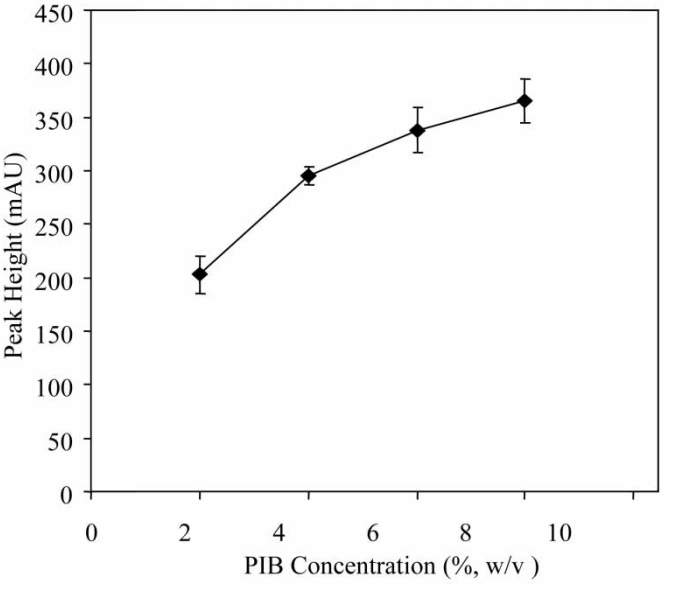

FIGURE 4 Effect of thickness of PIB on the detection of CN. A 6-g sample of soil containing 50 μg/g CN and 10% water was examined. Samples were heated to 90°C, and the evaporation/absorption time was 15 min. Spectra were obtained from the coaddition of 100 scans at a resolution of 4 cm^{-1}.

the PIB solution. As indicated in Fig. 4, the IR signal did not increase linearly with respect to the concentration of the PIB solution. This nonlinear behaviour is very likely to have been caused by the longer time needed for the analytes to penetrate into the inner zone of thicker polymeric films. Although the IR signal increased as the film thickness increased, the level of noise was also increased because of the attenuation of

the IR radiation as the film thickness increased. For thicker polymer films, the increase in the level of noise cancelled the positive effect of the increased IR signal. By performing an examination of the signal-to-noise ratio for PIB films of different thicknesses, the optimal PIB concentration in solution was determined to be around 6% (w/v). Therefore, a 6% solution was coated onto the aluminium plate in the following experiments.

Effect of Sample Volume

As indicated in Eq. (2), the volume of the headspace affects the amount of analytes that can be absorbed by the hydrophobic film. The relationships between the parameters in Eq. (2) are highly complex and are very difficult to simplify further. To practically examine the effect of the volume of the headspace in our proposed device, the amount of soil was varied, and the IR signals obtained after an absorption time of 10 min were plotted (Fig. 5). Because the volume of the sample vessel was fixed at around 20 mL, the increase in the amount of soil means that the volume of the headspace decreased. CN at 50 μg/g was used as the probe molecule, and the sample vessel was heated to 70°C. As can be observed in this figure, the amount of soil did not influence the intensity of the analytical signal significantly in the region examined. That is to say, the volume of the headspace had an insignificant influence on the analytical signals. This observation revealed that the products of $K_{fh} \times K_{hs} \times V_f$ and $K_{hs} \times V_h$ were smaller than V_s in Eq. (1) and, hence, could be omitted to obtain the following equation:

$$n^{\infty} = K_{fh} \times K_{hs} \times V_f \times C_o. \tag{3}$$

Because the analytical signal was not influenced significantly by the volume of the sample when the sample weight was greater than 6 g, this amount of soil was used for each of the following experiments.

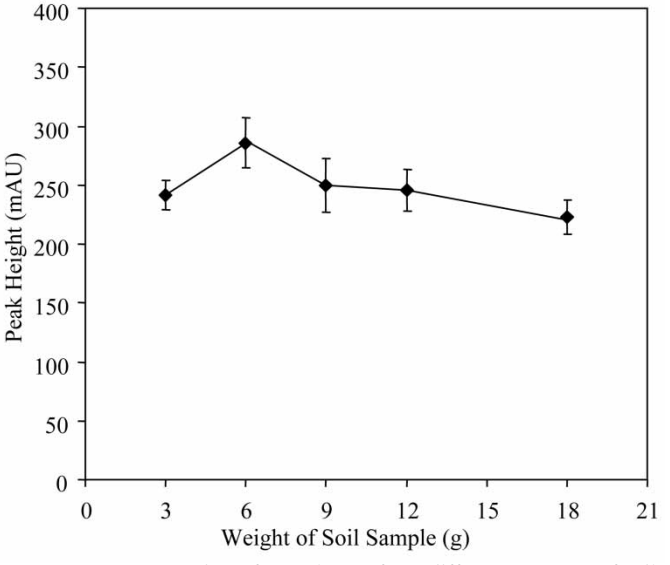

FIGURE 5 Detection of 50 μg/g CN from different amounts of soils.

Effect of Moisture

Soil samples usually contain small amounts of water. Basically, the presence of water in the soil can affect the analytical signals strongly because water molecules can interact with the active sites in the soils and, hence, cause the release of the organic compounds. To study the effect of water on the detection process, the soil samples containing 50 μg/g of CN were examined first. These samples were treated respectively with 0, 0.6, 1.2, and 1.8 mL of water, corresponding to 0, 10, 20, and 30% (v/w) water contents. When 20% water was added, the soil was completely covered with water. The heating temperature of the samples was kept at 90°C, and the IR signals obtained were plotted with respect to their evaporation/absorption times (Fig. 6). As can be observed in Fig. 6, a large increase in the signal was observed at a water content of around 10%. This finding indicated that water did help in releasing analytes from the soil matrix. Upon further addition of water to the soil, the IR signal decreased significantly. One explanation for this phenomenon is that water covered the soil completely, and therefore, the released analytes had great difficulty in reaching the interface between the soil and air. Meanwhile, the increased water content might have decreased the heating efficiency, which caused a delay in the time required for the analytes to experience the desired temperature in their environment.

To further study the effect of moisture, 6-g samples of soil containing 50 μg/g of CN were used. Different amounts of water were added into the soil samples. By keeping the heating temperature at 90°C and the sampling time at 10 min, the IR signals obtained were plotted and are presented in Fig. 7. As can be observed in this plot, the intensities of the analytical signals were maintained at a certain level for water contents in the region from 0.2 to 1 mL. This finding indicated that the analytical signals remained similar, provided that the water content was limited to an amount that did not cover the soil sample entirely.

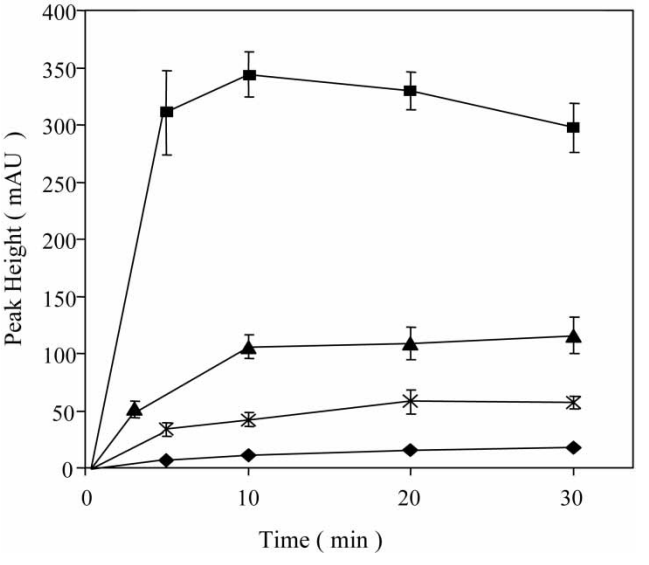

FIGURE 6 Extraction/absorption time profiles for soil samples containing 50 μg/g CN and 0 (◆), 10 (■), 20 (▲), and 30% (×) of water. One standard deviation based on triplicate runs is also plotted and is depicted by the error bars. The heating temperature was set at 90°C.

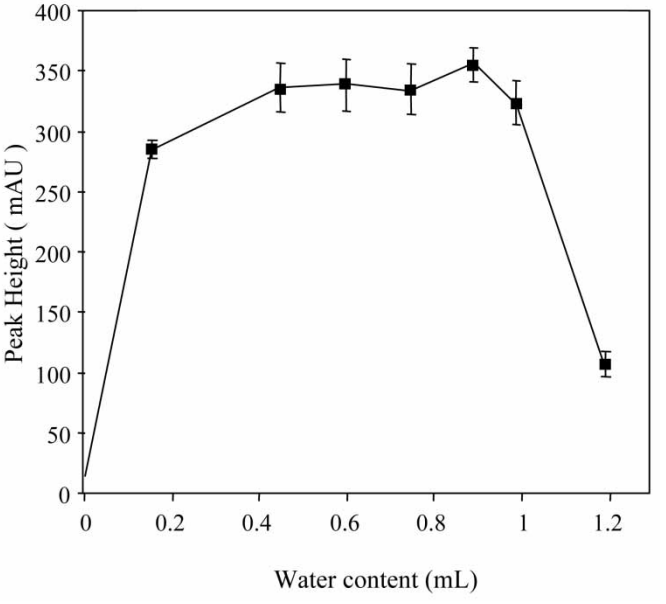

FIGURE 7 Effect of water content on the detection of 50 μg/g CN in 6 g of soil. The detection time was 10 min, and samples were heated at 90°C.

Effect of Temperature

Because the addition of thermal energy can increase the rate at which analytes escape from the soil matrix and into the headspace of the sample, the temperature effect was studied. The temperature range was varied from room temperature to 110°C. The soil samples were prepared to include 50 μg/g of CN and a water content of 10%. The evaporation/absorption time profiles for different temperatures were plotted (Fig. 8). As can be observed in this figure, the increase in the heating temperature affected the IR signals in a positive way, and the time required to observe maximum signals decreased. When the temperature was higher than 90°C, however, the detected signals were smaller than they were at a temperature of 70°C. This finding may have been caused by the warming of the hydrophobic film. Because the soil contained water, the temperature of the hydrophobic film could have been raised effectively by the water vapour at higher temperatures. This increase in the temperature of the hydrophobic film could be the main cause of the loss of the trapping efficiency for retaining CN in the film. Therefore, the signals decreased at higher temperatures.

Effect of the Volatility of the Analytes

To study the limitations of this method for the analysis of organic species in soils, six chlorinated aromatic compounds with different volatilities were examined: CN, PCB, TeCB, TCB, DCB, and CB; their vapour pressures were 0.017, 0.059, 0.067, 0.29, 1.0, and 12.05 Torr, respectively. CN was used as a surrogate for low-volatility compounds such as polyaromatic hydrocarbons, polycyclic biphenyls, and some chlorinated pesticides (e.g. DDT-type compounds), which, according to literature values, have a lower or similar vapour pressure to that of CN (0.017 Torr). The remaining compounds

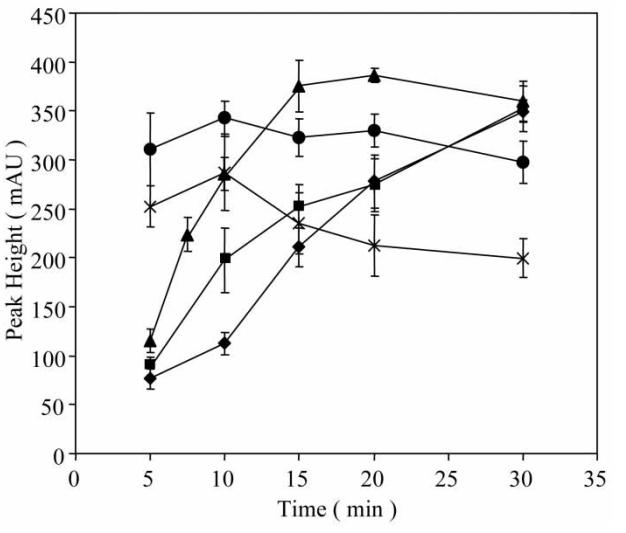

FIGURE 8 Extraction/absorption time profiles for the detection of 50 μg/g CN in soils containing 10% of water. Five temperatures were investigated: 50 (◆), 60 (■), 70 (▲), 90 (●), and 110°C (×). Spectra were recorded from the addition of 100 scans at a 4 cm^{-1} resolution.

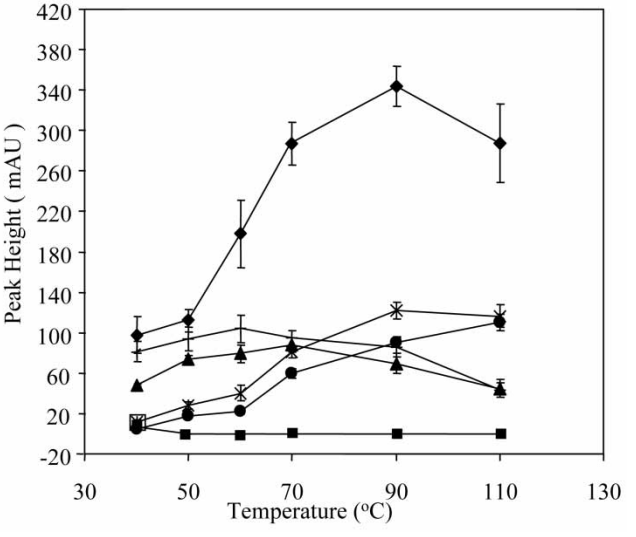

FIGURE 9 Effect of volatility of chlorinated aromatic compounds on the detection of the probe compounds (50 μg/g). The soils contained 10% of water. The examined compounds were CN (◆ ■), DCB (▲), TCB (+), TeCB (×), and PCB (●).

were used to determine the suitability of this method for the examination of medium- to high-volatility compounds that are commonly examined in soils. Using the method developed and described above, runs were performed using a concentration of 50 μg/g of each probe molecule in soil samples containing 10% of water. Each experiment was run in triplicate. In these experiments, a 6% PIB-coated aluminium cap was used. Spectra were collected by the co-addition of 100 scans at a resolution of 4 cm^{-1}. Figure 9 presents the IR signals obtained after an evaporation/adsorption time of

TABLE I Analytical results obtained for the probe molecules

Compound	*Vapour pressure* (Torr)	*IR signals* (mAU)[a]	*Detection limit* (ng/g)[b]	R^{2c}
1-CN	0.017	338.0 (±6.3)	42	0.995
1,2,3,4,5-PCB	0.017	90.3 (±5.0)	136	0.992
1,2,4,5-TeCB	0.074	121.7 (±6.5)	74	0.999
1,2,4-TCB	0.47	94.6 (±7.0)	112	0.994
1,2-DCB	1.0	90.0 (±4.6)	115	0.991
CB	12.05	7.0 (±6.0)	3142	–

[a]Chlorinated aromatic compounds (50 μg/g) were examined at a resolution of 4 cm^{-1}, and spectra were obtained from the coaddition of 100 scans. The evaporation/adsorption time was 10 min for all compounds examined. The heating temperatures were 90, 90, 90, 70, 70, and 40°C for CN, TeCB, PCB, TCB, DCB, and CB, respectively.
[b]Detection limits were calculated based on the ratio of the IR signals at 1 μg/g and at a peak-to-peak noise ratio of 3. The detection limit of CB was calculated based on the signals obtained at a concentration of 50 μg/g.
[c]The examined concentration was in the range of 1–50 μg/g.

10 min. As can be observed in this plot, the optimal temperatures varied for each of the compounds having different volatilities. For example, the IR signals of the low-volatility compounds, i.e. CN, TeCB, and PCB, increased as the heating temperature increased. For DCB and TCB, the maximum intensities of the IR signals were obtained at temperatures between 60 and 70°C. For high-volatility compounds, such as CB, lower temperatures provided higher-intensity signals in the examined temperature region. According to the analytical signals obtained for CB, this method was restricted to molecules with vapour pressures higher than that of CB. When considering the influence of water, temperatures lower than the boiling point of water were preferred so that the possibility of water condensing on the surface of the membrane was reduced. Therefore, in the analysis of semivolatile compounds in soil, the heating temperature is suggested to be optimal between 50 and 90°C.

Linearity and Detection Limits for Various Volatile Compounds in Soils

To examine the linearity between the intensities of the IR signals and their concentrations, 0.6 mL of water was added to soil samples containing different amounts of probe molecules. The results obtained are listed in Table I. As can be observed in this table, the linear regression coefficients (R^2) obtained for the examined compounds were all higher than 0.991 in the concentration range from 1 to 50 μg/g. For the detection of highly volatile compounds, such as CB, this method is generally limited by the high volatility. Therefore, no further examination of the linearity of the standard curve was performed. Based on the lowest concentration at which the signal-to-noise ratio was 3, the detection limits for chlorinated aromatic compounds exhibiting vapour pressures lower than 1.0 Torr were around 100 ng/g. This finding reveals that the developed method is highly suitable for the detection of low-volatility compounds.

CONCLUSION

In this article, a fast and simple method for the detection of chlorinated aromatic compounds in soil samples has been proposed. The PIB-coated sample cap effectively absorbed chlorinated compounds that had been vaporized from the soil samples. The time required for the detection was short, and in some cases was less than 10 min.

Increasing the amount of thermal energy allowed the analytes to be desorbed easier, and consequently, higher-intensity signals were obtained. However, because the hydrophobic film was warmed, the optimal heating temperature was around 70°C. Moisture present in the soils can effectively increase the rate of evaporation of the analytes. Within a 10-min sampling time, a high linearity of the standard curves existed, and low detection limits (around 100 ng/g) were readily achieved for chlorinated compounds with vapour pressures lower than 1.0 Torr.

Acknowledgements

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