FULL PAPER
THE ANALYST
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Development of an SPME/ATR-IR chemical sensor for detection of phenol type compounds in aqueous solutions

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Received 24th October 2000, Accepted 5th April 2001
First published as an Advance Article on the web 22nd May 2001

A new method, based on a combination of solid phase micro-extraction (SPME) and attenuated total reflection infrared (ATR-IR) spectroscopy, was developed for the detection of phenols in aqueous solutions. Several types of phenols were studied including phenols attached to methyl, hydroxyl, chlorine and nitro groups, which are environmentally toxic. Because of the polarity of the phenol-type compounds, the performance of six polymers in attracting phenols was investigated. Results indicated that poly(acrylonitrile-co-butadiene) was the most suitable SPME phase among the investigated polymers. To further increase the sensitivity in phenol detection, factors, such as the pH effect, salt effect and thickness of the SPME phase, were investigated. Results indicated that pH values affected the neutral form percentage of the analytes strongly and, hence, affected the detected signals. Due to the acid nature of phenols, phenol detection occurs best in solutions with a low pH value. A two- to three-fold increase in signals was observed after the addition of salt into the solution. The results on the examination of standard curve linearity indicated that the regression coefficients (R^2) were higher than 0.996 for four types of phenols. The obtained detection limits for phenols were lower than 200 μg L^{-1} for most of the compounds.

Introduction

Environmental scientists are very interested in phenols because of their toxicity.[1] For example, chlorophenols are toxic and suspected to be carcinogenic compounds.[2,3] Several sources can release these types of materials, such as manufacturing industries that produce dyes, antioxidants and drugs, and drinking water chlorination and chlorinated paper bleaching.[4,5] Because of the threat to the environment, methods were developed to provide a rapid and sensitive way to detect these compounds. For example, electrochemical detection methods have been applied for the detection of chlorinated phenols eluted using high performance liquid chromatography (HPLC).[6–10] Mass spectrometry has been also used to examine chlorinated phenols eluted using gas chromatography.[11] A surfactant-mediated extraction technique was also applied to the ultra-violet detection of chlorinated phenols eluted using HPLC.[12] Bachmann *et al.*[13] used microbial sensors to detect chlorinated phenols in aqueous solutions or organic solvents. Supercritical fluid extraction also has been applied to extract chlorinated phenols in river sediments.[14] Recently, the solid phase micro-extraction technique (SPME)[15–17] has been used to replace the steps in conventional sample pretreatment so that sampling, extraction and concentration are integrated into one step. Large numbers of applications based on SPME/chromatographic methods can be found in the literature. Although the steps in sample analysis are largely reduced by using SPME, the speed of sample analysis is still limited by the chromatographic separations.

Unlike chromatographic methods, the organic analytes in aqueous solutions can be detected rapidly using infrared sensing methods. This advantage allows the screening and removal of unsuspected analytes in environmental samples in a very short time. The attenuated total reflection infrared (ATR-IR) spectroscopic method[18] was found to be highly suitable for the detection of analytes in aqueous solutions.[19–23] ATR is suitable for managing aqueous solutions because the evanescent wave penetrates into the adjoining medium for a short distance. This can eliminate spectral interferences from the water. The depth of penetration, d_p, of the evanescent wave is calculated according to the following equation:

$$d_p = \lambda/\{2\pi n_1[\sin^2\theta - (n_2/n_1)^2]^{1/2}\} \quad (1)$$

where θ is the angle of incident, λ is the wavelength of the incident radiation, n_1 is the refractive index of the internal reflection element (IRE) and n_2 is the refractive index of the sample material. In the mid-infrared range, d_p varies from 0.1 μm to approximately 1 μm. A further increase in sensitivity in organic compound detection in aqueous solutions was observed by applying SPME to the ATR-IR method.[24–31] When a hydrophobic material, with a thickness close to d_p, is coated onto the surface of the IRE, analytes are absorbed into the hydrophobic film and sensed by IR radiation. The principle of the SPME/ATR-IR method is the same as for SPME in the absorption of analytes in aqueous solutions. Because the SPME principle can be found easily in the literature, only a brief description will be given here.

The partition coefficient in a two-phase system is of great concern in SPME. The partition coefficient can be expressed as the ratio of the concentration of solute in the hydrophobic phase to the concentration in the aqueous phase as shown in eqn. (2):

$$K = C_{org}/C_{aq} = [(n_o/V_f)]/[(C_o \times V_s - n_o)/V_s] \quad (2)$$

where K is the partition coefficient, C_{org} is the analyte concentration in the hydrophobic layer, C_{aq} is the solute concentration in the aqueous phase, n_o is the number of analyte molecules in the organic layer, V_f is the volume of the hydrophobic layer, V_s is the volume of the aqueous solution and C_o is the initial concentration of the analytes in the aqueous sample. By assuming that the sample volume, V_s, is much larger than $K \times V_f$, eqn. (2) can be rearranged and expressed in a simple form:

$$n_o = K \times V_f \times C_o \quad (3)$$

This equation indicates that the larger the volume of the hydrophobic film, the larger the signal that can be obtained. Quantitative results can be obtained for SPME under non-

equilibrium conditions based on the following equation as derived by Ai:[32]

$$n = n_o \times [1\text{-}\exp(- a \times t)] \quad (4)$$

where t is the equilibrium time and parameter a is a measure of how fast the adsorption equilibrium can be reached in the SPME process. This equation can be used to monitor the analytical signals under non-equilibrium conditions.

Commonly used materials for SPME phases, such as low-density polyethylene (LDPE),[23] poly(vinyl)chloride (PVC),[26] and polyisobutylene (PIB)[29] are low in polarity. Due to their low polarity, these materials are only suitable for attracting organic compounds of relative low polarity in aqueous solutions. To apply this method to detect phenols, the polarity of the hydrophobic film must be increased to increase the phenol partition coefficients. The SPME phases should also be within the IR absorption range to decrease the spectral interference. Their water solubility should be low to increase their stability in aqueous solutions. The SPME phase should be low in compactness to attract phenols at a relatively high speed. To meet these requirements for SPME phases in the detection of phenols using the SPME/ATR-IR method, commercially available polymers containing phenyl- and cyano groups were considered and examined in this work. Because both phenyl- and cyano groups can have a strong interaction with phenols either by π–π interactions or dipole–dipole interactions, the attraction capabilities are expected to be higher than low-polarity polymers. Therefore, polystyrene (PS) and polyacrylonitrile (PA) were studied first. In terms of spectral interference, PA is more suitable than PS because the cyano group exhibits an infrared absorption band (around 2237 cm^{-1}) in the region in which most organic compounds have no absorption. To increase the analyte transportation speed in the SPME phase, the polymer compactness should be sufficiently low. Copolymers, such as polyacrylonitrile-co-butadiene (PAB) and polystyrene-co-butadiene (PSB), were selected for this purpose. To have a fair comparison, the commonly used PIB and PVC polymers were also used in this work.

Experimental

Materials and reagents

The performance of six polymeric materials were studied for phenol absorption. These materials included PIB, PVC, PA, PS, PAB and PSB, and were obtained from the Aldrich Corp. (Milwaukee, WI, USA). Phenols used in this work included phenol, 4-chlorophenol (4-CP), 2,3-dichlorophenol (2,3-DCP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 3,4-dichlorophenol (3,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2-methylphenol (2-MP), 4-methylphenol (4-MP), 4,6-trimethylphenol (2,4,6-TMP), 3-hydroxylphenol (3-HP), 2-hydroxylphenol (2-HP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP). Acetone was used to dissolve PAB, and PAS. Toluene was used to dissolve PIB, PS and PSB. Dimethylsulfoxide was used to dissolve PA. These solvents were obtained from TEDIA (Ohio, USA) as reagent grade.

Procedure of SPME coating

1 to 5% (w/v) PAB solutions were prepared by dissolving PAB in acetone. Hydrophobic film-coated IRE was obtained by soaking the ZnSe crystals in the PAB solution directly and air-drying for one hour. Based on integrated peak intensities of around 2237 cm^{-1}, the average relative standard deviation of the PAB film thickness for four replicated runs in four different PAB solutions was 5.04%.

Sampling and detection procedure

A 45° trapezoidal (55 × 25 × 2 mm) zinc selenide crystal (ZnSe), purchased from the International Crystal Laboratory (Garfield, NJ), was cut into 3 mm (55 × 3 × 2 mm) widths and used as the IRE. The sample cell setup was arranged as shown in Fig. 1. The dimensions of the sample cell were 2.8 × 2.8 × 12.5 cm^3. The IRE (45° trapezoidal ZnSe) was placed in the sample cell and located around 5 cm from the top. This cell was placed into the sample compartment for direct IR signal measurements. A magnetic stirrer was used to accelerate the extraction process. Because the magnetic stirrer did not fit into the sample compartment, the sample cell was moved out of the sample compartment for stirring. A Jasco 410 FT-IR spectrometer equipped with a medium-range mercury–cadmium–telluride (MCT) detector was used to detect the absorbed analytes. Probe organic compounds were dissolved in water to form the desired concentrations. A 70 mL portion of the sample solution was placed into the sample cell for measurement. All of the spectra were collected by co-adding 100 scans with 4 cm^{-1} resolution. Fig. 2 shows typical spectra obtained using PAB as the SPME phase.

Results and discussion

Effect of hydrophobic film in the detection of phenols

Six polymers were studied for their performance in phenol absorption. In terms of functionality, four types of polymers can be distinguished including non-polar (*i.e.*, PIB), chlorine attached (PVC), phenyl group attached (PS and PSB) and cyano group attached (PA and PAB). PIB and PVC have low compactness and have been fully studied in the literature. The copolymers, PAB and PSB, should also exhibit lower compactness than PS and PA because it is more difficult to pack these polymers in order. Polymer solutions in 3% (w/v) were used to coat the ZnSe crystal and ATR spectra were then measured. To study the performance of these polymers in the absorption of phenols, 2,3-DCP was used as the probe molecule. Spectra were collected through the absorption of 70 mL of probe molecules at a concentration of 100 mg L^{-1} for 20 min. Based on absorption peak intensity of 2,3-DCP located at 906 cm^{-1}, the obtained IR signals using different polymers are shown in Fig. 3A. As can be seen in this figure, highly compact polymers, such as PA and PS, have weak IR peak intensities. This is caused by the slow diffusion of analytes into the compacted polymer phases. PIB and PVC have low compactness but lack a suitable polar functional group, which leads to low IR signals. The low-compact polar polymers (*i.e.*, PSB and PAB) showed different

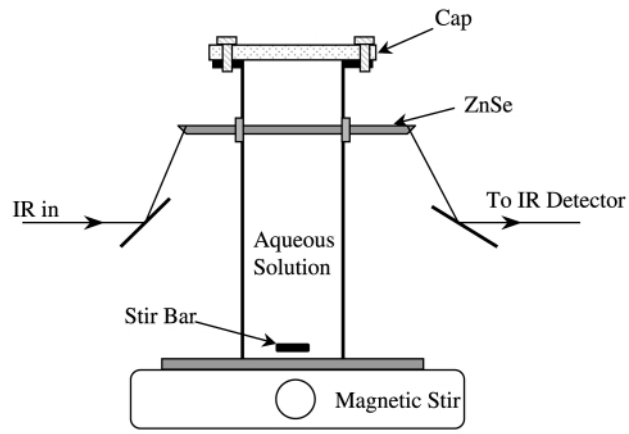

Fig. 1 Structure of the liquid cell and optical arrangement used in this work.

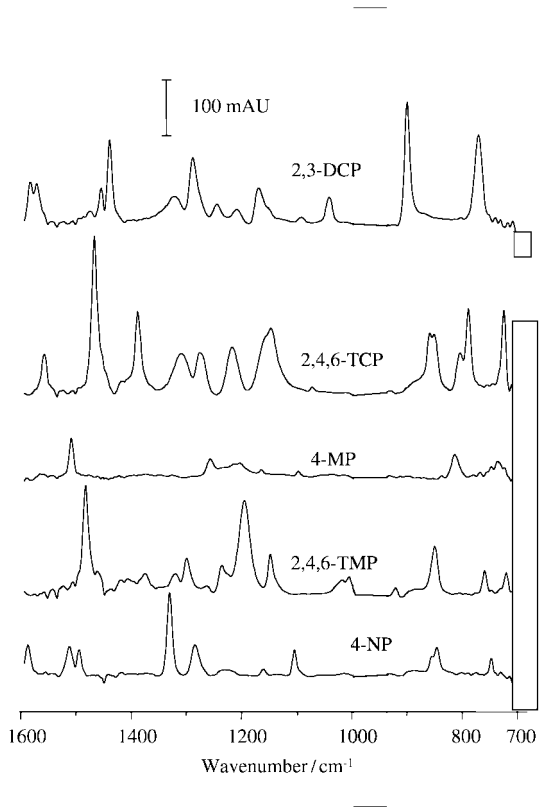

Fig. 2 Typical detected spectra of four different types of compounds in 100 mg L^{-1} of aqueous solutions.

capabilities in the adsorption of 2,3-DCP. Because the diffusion speeds were similar in these three polymers, the difference in IR signals was caused mainly by the functionality of the attached groups. The observed IR signals showed that PAB has a very high IR signal but PSB has a peak intensity of half of PAB. This may be because the interaction between the cyano group and phenol is stronger than between the phenyl group and phenol. To verify that PAB is the most suitable SPME phase for phenols, 4-NP, 4-MP and 3-HP were further examined using both PAB and PSB as SPME phases. Results are plotted in Fig. 3B. The peak positions for the examined compounds were 1337 cm^{-1}, 1515 cm^{-1}, and 1147 cm^{-1}, for 4-NP, 4-MP and 3-HP, respectively. As can be seen in this figure, the IR signals of these three types of phenols were higher using PAB than using PSB. This proves that PAB is more suitable for phenol compound detection than the PSB polymer. Therefore, PAB was used as the SPME phase in the following analyses.

Determination of SPME film thickness and stability in aqueous solutions

As discussed above, PAB was the most suitable hydrophobic film for phenol absorption. To determine the most suitable thickness for ATR-IR chemical sensor absorption, PAB solutions of 1 to 5% (w/v) were prepared. After placing a PAB coating on the surface of the IRE, the PAB spectra were collected. Fig. 4A shows the results obtained by plotting the peak intensity of the −CN stretching bond located at 2237 cm^{-1} against that of the PAB solution concentration. As can be seen in this figure, the peak intensity increased as the PAB solution concentration increased, but reached a maximum value when 3% PAB was used. This is because the PAB thickness is close

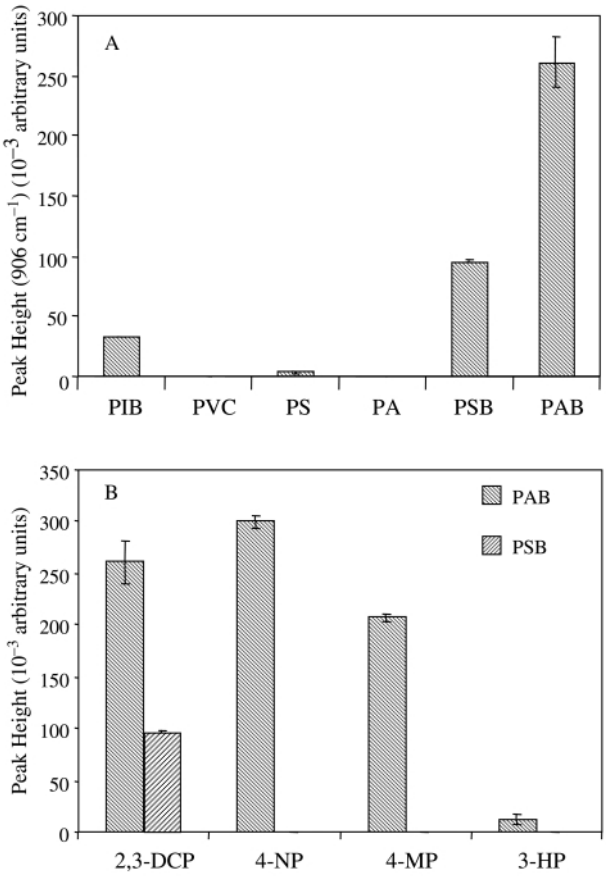

Fig. 3 A, detected IR signals of 100 mg L^{-1} of 2,3-DCP using six SPME phases, PIB, PVC, PS, PA, PSB and PAB. B, detected IR signals for four compounds at a concentration of 100 mg L^{-1}. Both PAB and PSB were used as SPME phases.

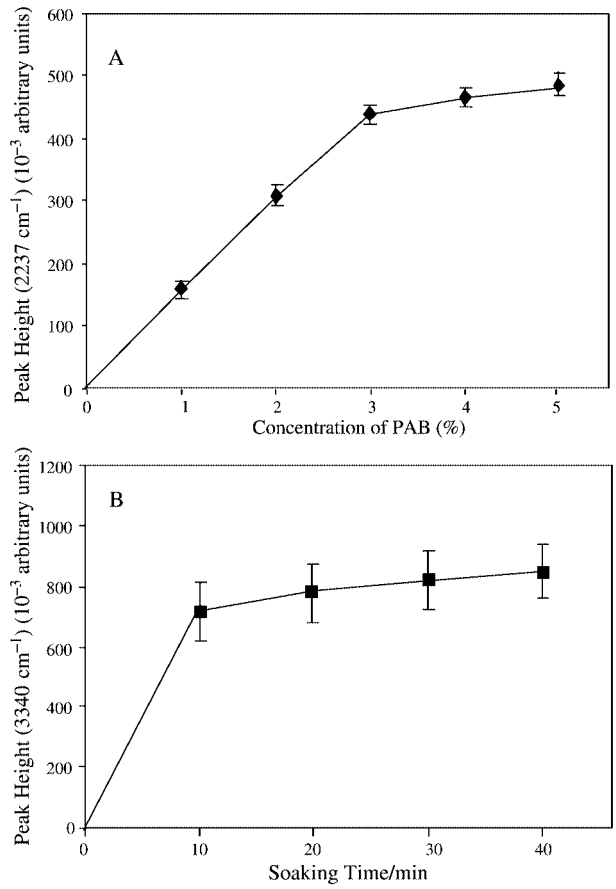

Fig. 4 A, IR signals of PAB against the concentrations of the coating solutions. B, variation of IR signals of water after soaking PAB-coated IREs in water.

to d_p. The standard deviation for this coating procedure was less than 5%, as seen in Fig. 4A. As the SPME phases should be stable enough to obtain consistent data, a coated ATR crystal was placed in water for a certain period of time and the polymer absorption peak intensity was monitored. The CN peak intensity slightly decreased to a certain value (10% decrease of the CN signal) after soaking the polymer in an aqueous solution for 40 min. This may be because the polymer was partially removed from the ZnSe crystal. However, after the coated crystal was removed from the aqueous solution and dried with an electrical fan for 20 min, the CN peak intensity returned to the original value. Therefore, we believe that the refractive index of the polymer film was changed by the water molecules that penetrated into the coating, and this was responsible for the decrease in peak CN intensity. The peak intensity for the water absorption was monitored at around 3500 cm^{-1}, as shown in Fig. 4B. The water absorption band changed rapidly after the aqueous solution penetrated, and the peak intensity slowly increased after 10 min.

Absorption time profiles

To study the speed of phenol detection, 2,3-DCP was used as the probe molecule and its absorption–time profile was obtained by plotting the peak intensity of 2,3-DCP at 906 cm^{-1} against the absorption time. Two conditions were used, with and without sample solution stirring. The absorption–time profiles are plotted in Fig. 5A and the corresponding results from eqn. (4) are tabulated in Table 1. As can be seen in this figure, the time to reach 80% of the maximum signals was around 20 min and the time was slightly reduced by stirring the sample solutions. To study the effect of salt addition, different amounts of NaCl were added to 100 mg L^{-1} of a solution of 2,3-DCP. The obtained IR signals are plotted against the soaking time in Fig. 5B. As can be seen in this figure, the IR signals increased greatly after soaking the sample solution for 60 min. The analysis time should in practice be shorter than 20 min. As can also be seen in Fig. 5B, the IR signals at 20 min of absorption time were very similar with or without the addition of NaCl. This reveals that the addition of NaCl to the sample solution can effectively increase the sensitivity of equilibrium conditions, but has less influence on the sensitivity of phenol detection if the system is operated under non-equilibrium conditions. The corresponding fitted results from eqn. (4) are also tabulated in Table 1 for easier comparison.

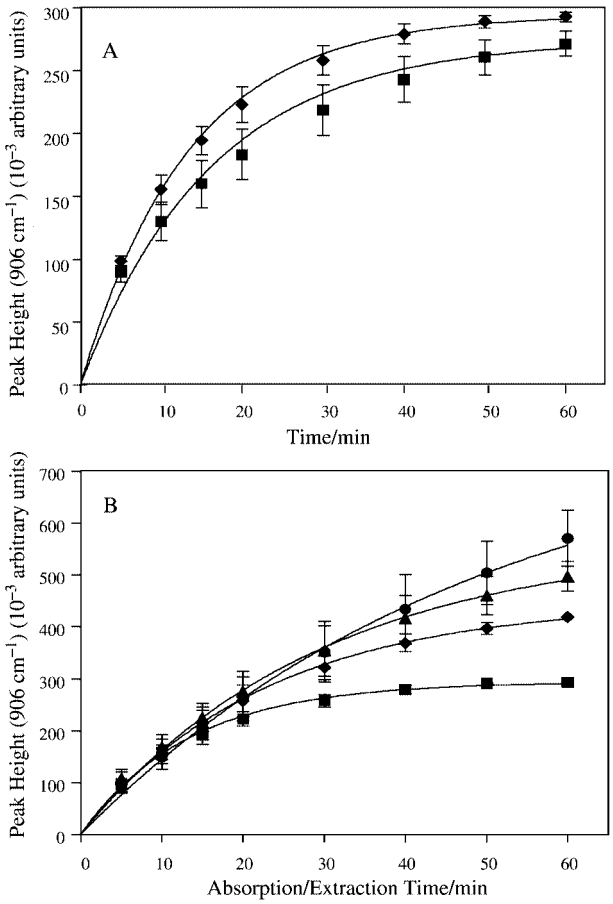

Fig. 5 A, Absorption–time profiles for 100 mg L^{-1} of 2,3-DCP with (◆) and without stirring (■) B, absorption–time profiles after addition of NaCl; 0% (■), 5% (◆), 10% (▲), 20% (●).

Effect of pH on chlorophenol determination

Because phenols contain the hydroxyl group, which acts as an acid in aqueous solutions, the pH of the sample should be considered in order to increase the detection speed. When phenols dissolve in water, a portion of the phenols will be in a charged form. This charged form of phenols reduces the capability of the hydrophobic film to attract the chemicals. To obtain the optimal analytical conditions, the pK_a of the phenols was estimated based on the Hammett equation.[1] This equation can be expressed as:

$$pk_a(\text{phenols}) = pK_a(\text{phenol}) - \rho \sum_i \sigma_i \qquad (5)$$

where ρ is the susceptibility factor and σ is the Hammett constant. For phenol, pK_a is 9.92 and ρ is 2.25. The values of σ for different functional groups at any position can be easily obtained from the literature.[1] According to eqn. (5), the pK_a values for the examined phenols were calculated and the results are listed in Table 2.

Based on the estimated pK_a values, the free form of phenols at any pH can be calculated. As can be seen in Table 2, the neutral form of most phenols is higher than 90% for a pH controlled at a value lower than 6. For phenols with a pK_a lower than 7, the neutral form percentage at pH = 6 is less than 90%. If the solution is not pH controlled, the percentages of neutral form phenols will be concentration related. Because of the low concentration of analytes, the pH value should be close to 7 for low phenol concentrations. For phenols with a pK_a higher than 7, this effect is smaller because most analytes are in the neutral form. To study this effect, 4-MP, 2,3-DCP, 2,4,6-TCP, and 2,4-NP were used as probe molecules and their pK_a values were 10.30, 7.56, 6.34 and 5.38, respectively. Solutions were prepared at a concentration of 100 mg L^{-1}. These solutions were tested with and without pH adjustments. The pH values of the sample solutions were adjusted by addition of HCl and NaOH to 4, 6 and 8. 2,3-DCP was first examined to obtained the

Table 1 Fitted coefficients of *k* and *a* in eqn. (4)

Conditions	*k*	*a*
Effect of Stirring:		
No stir	260	0.068
Stir	294	0.075
pH Effect:		
Not adjusted	294	0.075
pH = 4	319	0.067
pH = 6	279	0.061
pH = 8	108	0.067
Addition of NaCl:		
0%	294	0.075
5%	447	0.044
10%	564	0.034
20%	798	0.020

influence of pH on the absorption/extraction time profiles. Eqn. (4) was used to fit the obtained time profiles and the results are tabulated in Table 1. As can be seen in this table, the k coefficient in eqn. (4) is strongly influenced by pH. This reveals that the amount of 2,3-DCP partitioned into the SPME phase varied with the pH value. However, the speed of penetration into the SPME phase was not influenced by pH, because the coefficient a was very similar for different pH values. To further explore this behavior, other compounds were also examined and the results of the obtained IR signals after soaking in the sample solution at a concentration of 100 mg L^{-1} for 20 min are tabulated in Table 2. As can be seen in this table, for compounds with pK_a larger than 7, the IR signals for solutions without any pH adjustment are very close to the signals for solutions adjusted to low pH values. For compounds with pK_a smaller than 7, the obtained signals varied largely at different pH values. Therefore, for determination of compounds with low pK_a, solutions should be pH controlled.

Linearity and detection limits in the determination of chlorophenols

More than ten phenols were examined for their standard curve linearity and sensitivity. Table 3 lists the signals of these compounds using a 3% PAB-coated IRE to absorb concentrations of 1 to 150 mg L^{-1} of each compound. The absorption/extraction time was 20 min in these runs. As can be seen in this table, the obtained IR signals were very intense for most of the compounds, especially for chlorophenols. The IR signals of three compounds, phenol, 4-HP and 2,4-DNP, were very weak. This may be caused by the low partition coefficient for PAB to absorb these high polarity compounds. Based on three times the noise level, the calculated detection limits for these chlorophenols are also tabulated in Table 3. Detection limits were lower than 200 μg L^{-1} for most of the compounds but higher than 2 mg L^{-1} for the three high polarity compounds. The regression coefficients of the five compounds were higher than 0.996. This indicated that this method was very suitable.

Analyses of real water samples

As a preliminary test to determine whether real water matrices interfered with these extractions, each of the analytes was spiked into two types of water to form concentrations of 10 mg L^{-1} of analytes. Creek water was obtained in a creek located in the northern part of Taiwan (Old Street Creek). The underground water was obtained by pumping underground water (located in the campus of Chung-Yuan Christian University, Taiwan) from roughly 30 feet below the ground surface. After evaporation in air, the residual concentrations in the creek and underground waters were 156 and 136 mg L^{-1}, respectively. Because the pH of the aqueous sample can influence the extraction efficiency strongly, the pH values of the water matrices were also examined and found to be 6.7 and 6.1 for the creek and underground waters, respectively. To eliminate the pH effect, all of the water samples were buffered using 0.01 M potassium biphthalate, which has a pH value around 3.97. Buffered de-ionized water was used for analytical signal comparison. The calculated recovery data defined as the ratio of signals from real water samples to that of de-ionized water are shown in Table 4 along with the RSDs of the measurements. The percentage RSDs were obtain from triplicate measurements in these water matrices. As can be seen in Table 4, the recoveries were good, ranging from 95 to 103%. The solid matter in the water sample did not significantly affect the extraction recoveries for the examined phenols.

Regeneration of SPME phase

The SPME phases can be easily regenerated. The performance of water was examined in removing the absorbed 2,3-DCP and 4-NP out of the SPME phase. The obtained IR signals showed that, after soaking the absorbed SPME phase in water for 20 min, the IR signals decreased to about 25% of the original signal. If the water contained 5% methanol, the speed of regeneration increased slightly and the residual signal was around 10% for 20 min of regeneration. The speed in removing analytes was also dependent upon which analyte was absorbed. For example, for removing 4-NP out of a PAB phase, the

Table 2 Calculated pK_a values and obtained IR signals for five phenols measured at different pH. Absorption time was 20 min for all the measurements

Compounds	pKa	Compounds	pH	IR signal/mAU
2,4,6-TMP	10.89	4-MP	No adjustment	68.63 (±2.39)
2-MP	10.21		4	68.97 (±3.98)
4-MP	10.30		6	66.97 (±2.10)
3-HP	9.70		8	67.53 (±0.90)
2,4-DNP	5.38			
4-NP	8.17	2,3-DCP	No adjustment	222.9 (±14.1)
Phenol	9.92		4	232.9 (±12.5)
4-CP	9.40		6	196.4 (±18.3)
2,3-DCP	7.56		8	78.6 (±4.6)
2,4-DCP	7.87			
2,6-DCP	6.86	2,4,6-TCP	No adjustment	119.5 (±4.0)
3,4-DCP	8.57		4	140.0 (±8.2)
2,4,6-TCP	6.34		6	70.5 (±5.5)
			8	7.3 (±0.3)
		2,4-DNP	No adjustment	13.9 (±0.4
			4	21.0 (±2.5)
			6	Undetectable
			8	Undetectable

Table 3 Obtained analytical signals for examined phenols based on 20 min of extraction/absorption time

Compounds	IR Signals[a]/ mAU	Peak position/ cm^{-1}	Detection limit[b]/ μg L^{-1}	R^{2d}
2,4,6-TMP	455.6 (±2.8)	1488	103	0.9964
2-MP	109.2 (±2.4)	1107	602[c]	
4-MP	207.5 (±3.8)	1515	241	0.9999
3-HP	12.0 (±4.5)	1147	5475[c]	
2,4-DNP	34.2 (±4.4)	1265	1921[c]	
4-NP	300.0 (±7.1)	1337	447	0.9998
Phenol	32.9 (±3.0)	1501	1999[c]	
4-CP	172.6 (±0.5)	1267	227	
2,3-DCP	261.0 (±20.1)	906	154	0.9960
2,4-DCP	298.1 (±13.1)	1287	149	
2,6-DCP	120.1 (±3.6)	1319	547[c]	
3,4-DCP	294.5 (±14.6)	1286	207	
2,4,6-TCP	195.1 (±11.4)	1395	517	0.9972

[a] 100 mg L^{-1} samples containing 20% (w/v) of NaCl were examined. [b] Detection limits were estimated from the signals of analytes at a concentration of 1 mg L^{-1} (three times the peak-to-peak noise level). [c] Detection limits were estimated from the signals of analytes at a concentration of 10 mg L^{-1}. [d] No addition of NaCl, and detection time of 20 min.

Table 4 Recoveries (20 min) for three phenols spiked into real water matrices

	% Recoveries (%RSD)[a]	
Chemicals	Creek Water	Underground Water
4-NP	99.3 (6.8)	101.3 (3.0)
2,3-DCP	103.9 (1.3)	103.7 (4.6)
2,4,6-TMP	95.0 (6.4)	99.4 (3.4)

[a] RSD (%) data obtained from triplicate extractions of 10 mg L^{-1} analytes.

residual signals were close to 5% after soaking in water for 20 min. Using the regenerated sample to absorb analytes, less than 3% of the standard deviation could be obtained.

Conclusion

In this study, the SPME/ATR-IR method was used to detect phenol compounds. The use of the PAB as the SPME phase was the essential element in the success of this method in phenol detection. This polymer has been compared to other commonly used polymers and some commercially available polymers. The investigated results indicated that PAB was much more suitable for the attraction of phenols. To increase the sensitivity in the detection of phenols, both the pH and salt effects were studied. As the results indicated, a pH lower than 7 is suggested for detection of phenols due to the acidity of this type of compound. The salt can increase the IR signals. However, in terms of speed of analyte detection, the slow speed in reaching equilibrium limits the use of the salting out effect. The results from examination of the standard curve linearity indicated that the regression coefficients (R^2) are higher than 0.996 for four types of phenols. The obtained detection limits for phenols are lower than 200 $\mu g\ L^{-1}$ for most of the compounds. However, sensitivity was relatively low for high- polarity compounds, such as phenol, 4-HP and 2,4-DNP. In the analysis of real water samples, the recoveries for two kinds of water spiked with different phenols ranged from 95% to 103%. This indicates that the water matrix did not significantly influence the analytical signals.

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. NSC89-2113-M-033-009.

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