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# Poly(dimethylsiloxane) films as sorbents for solid-phase microextraction coupled with infrared spectroscopy

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**Abstract**

Poly(dimethylsiloxane) (PDMS) film was investigated as a stationary phase for solid-phase microextraction coupled with infrared (IR) spectroscopy. Five organic compounds of environmental concern (trichloroethylene, perchloroethylene, *o*-xylene, *p*-xylene, and trifluralin) were selected as test compounds for this study. Spiked solutions were extracted from 250-ml water samples into small squares (3.2×3.2 cm) of commercially available, 127-μm thick, PDMS film. The equilibration times for the test analytes in PDMS ranged from 60 to 85 min, and were about three times faster than those in Parafilm M. However, it was found that PDMS had poorer detection limits (in the range of 0.2–4.4 ppm) than those obtained with Parafilm M (in the range of 0.066–1.8 ppm). The relative standard deviations of the measurements were from 6.7–12%, and were governed primarily by volatility losses. Finally, preliminary work with PDMS demonstrates that real water matrices do not adversely affect the detection of organic compounds. 

*Keywords:* Poly(dimethylsiloxane) film; Parafilm; Solid-phase microextraction; Extraction methods; Trifluralin; Xylenes; Chloroethylenes

## 1. Introduction

Solid-phase microextraction (SPME) is a solventless method used to selectively extract organic compounds from aqueous solutions. The most common application of SPME is in gas chromatography, where the solid phase is coated on a fiber held in a modified syringe device [1]. In this application, the solid phase (on the fiber) is exposed to the water solution to allow an equilibrium to be reached between the concentration of the organics in the aqueous phase with that in the solid phase. Once equilibrium has been attained, the fiber is removed from the solution and the organics are thermally desorbed from the solid phase in the injector of a gas chromatograph. Extractions are primarily based on the polarity match of the solid phase to those of the compounds of interest.

Recent work in our laboratory has focused on coupling optical transmission spectroscopy with SPME [2–5]. In our application, a film or rectangular chip of the solid-phase material is used to preconcentrate organic compounds from water similarly as in the application of SPME with GC. However when using optical spectroscopy as the detector, the partitioned organics are then directly determined in the solid phase through the Beer–Lambert law:

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$$A = \epsilon bc \quad (1)$$

where $A$ is the absorbance, $\epsilon$ is the molar absorptivity, $b$ is the pathlength, and $c$ is the concentration. As opposed to detecting the organics directly in solution, applying SPME preconcentration to optical spectroscopy removes the water and matrix interferences which makes it possible to detect organic contaminants in the ppb–ppm range [5].

Of the various optical spectroscopic detection methods investigated as detectors for SPME, infrared (IR) spectroscopy is the most useful because it provides species-specific information through molecular vibrations. For example, Heglund and Tilotta developed a simple and inexpensive method for the detection of 10 volatile organic compounds (VOCs) in water through SPME–IR using Parafilm M (The American National Can Company, Norwalk, CT, USA) as the solid phase [5]. Although detection limits in the ppb to low ppm range were obtained for the VOCs studied, the equilibration times were long, up to 200 min. Wittkamp et al. developed a method for determining aromatic components in water using SPME coupled with ultraviolet absorption spectroscopy [3,4]. This method, which uses a small chip of poly(dimethylsiloxane) (PDMS) as the solid phase, provided detection limits in the low ppb range with relatively short equilibration times (in the range of 30–100 min). Unfortunately, due to broad analyte absorption bands in the UV, this method is also only selective for total aromatic compounds. Additionally, the solid-phase chips were fabricated in the laboratory which was tedious and time consuming.

The purpose of this study was to investigate the utility of PDMS as a solid phase for SPME–IR. PDMS is the most common solid phase used in the syringe devices thus far, and also has shown utility as an effective sample preconcentrator in sorptive extraction–thermal desorption (SE–TD) chromatography [6–9]. PDMS films, commonly used as cell growth membranes, are relatively inexpensive and can be commercially obtained suitable for IR transmission spectroscopy in 127-μm thick sheets. For this study, five environmentally important compounds were selected in order to characterize the PDMS as a solid phase when IR spectroscopy is used as a detector. Four of the compounds were previously studied using Parafilm M, making possible a comparison of the performance of the two films. Useful analytical bands, calibration data, distribution constants, and standard deviations were determined for each of the compounds.

## 2. Experimental

### 2.1. Reagents

All chemicals were spectrophotometric grade and were used as obtained from Aldrich (Milwaukee, WI, USA). Trifluralin (99% purity) was purchased from Chem Service (West Chester, PA, USA). Stock solutions of the various organic compounds were prepared by spiking the appropriate amount of the compound into methanol and then diluting with distilled water. The final methanol concentration did not exceed 0.4% of the solution volume. Calibration solutions were prepared from the stock solution, and all solutions were used within 30 min to avoid analyte evaporative losses. A sample of uncontaminated water was obtained from Lake Lamond in Bagley, MN, USA.

### 2.2. Solid-phase film and extraction apparatus

PDMS film (Specialty Manufacturing, Saginaw, MI, USA), 127-μm thick, was used to extract the organics from water. Square extraction films, 3.2 cm on an edge, were cut from the silicone sheet and four 6-mm diameter holes were punched in order for them to be placed in the aluminum holders as described previously [5]. The resultant volume of the film was calculated to be 115.7 $mm^3$. The films were conditioned prior to use by rinsing them with a mixture of methanol–water (50:50). Additionally, each film was reconditioned before reuse by soaking it in the methanol–water solution for 5 min with stirring. For both cases, the methanol–water solution was allowed to evaporate as evidenced by the lack of methanol bands in the IR spectra of the films.

The glass extraction vessels (which held 250 ml of solution) and aluminum film holders were identical to those used in a previous study [5]. Six film holders were used so that parallel extractions could be performed. As shown in a previous study, the rate

of partitioning of the analytes into the solid phase is greatly affected by the solution stir rate (agitation) [10]. However, the stir plates used in this work were not all the same brand and the stir bars were not uniform in size. Therefore in order to stir all the samples at similar rates, the height of each vortex was measured and the stir rates were adjusted until the heights were all similar. Of course, the stir rates were limited by that obtained on the slowest stir plate.

### 2.3. Instrumentation

A standard Mattson Genesis Fourier transform infrared (FT-IR) spectrometer (Madison, WI, USA) was used to obtain IR spectra of the organic compounds in the films. The spectrometer was equipped with a room temperature deuterated triglycine sulfate detector (DTGS). All spectra were obtained at a scan rate of 6.25 kHz, 4 $cm^{-1}$ resolution, and triangular apodization. Thirty-two scans were co-added for both the sample and the background spectra. Infrared absorbance spectra of pure compounds in $CS_2$ were obtained in triplicate using a Zn–Se cell with a pathlength of 206 μm.

### 2.4. Procedures

IR spectra of the organics partitioned into the solid-phase films were acquired as follows. After conditioning, a reference single-beam background spectrum of the film was acquired and saved. Quickly following the extraction, the sample single-beam spectrum of the film was taken. The absorbance spectrum of the analyte was then obtained by ratioing the sample single-beam spectrum to the saved background single-beam spectrum.

Minimum sample evaporative losses were assured by tightly capping the extraction jars and handling the films quickly after the extraction procedure. Removing the films from the extraction jars and drying them took approximately 5 s before being placed in the FT-IR spectrometer.

Detection limits were defined as that analyte concentration required to produce an absorbance equal to $10\sigma$ of the peak-to-peak baseline noise.

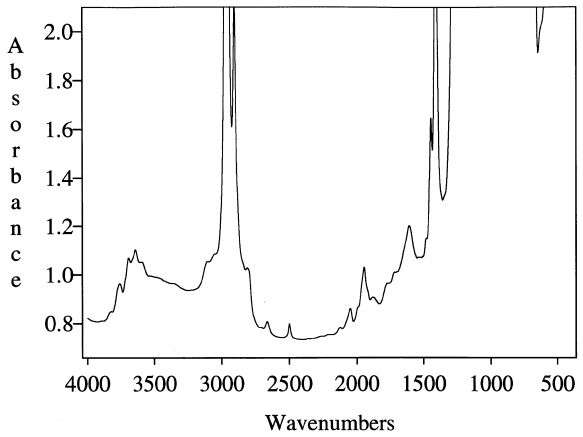


Fig. 1. Infrared absorption spectrum of 127-μm thick poly(dimethylsiloxane) film.

## 3. Results and discussion

### 3.1. Infrared windows of PDMS

Fig. 1 shows an IR absorbance spectrum of the PDMS film in the region of 4000–400 $cm^{-1}$. The characteristic absorptions from aliphatic CH stretching (3000–2840 $cm^{-1}$), methyl group bending (1375–1450 $cm^{-1}$), methyl group stretching (2962 and 2872 $cm^{-1}$), and $CH_3Si$ stretching at (1300–1280 $cm^{-1}$) and (875–750 $cm^{-1}$) makes these regions opaque [11]. The useful spectral regions in PDMS are >3035, 2768–1470, 1408–1289, 958–906, 745–714 and 658–523 $cm^{-1}$. It should be noted that Parafilm M, the other useful solid-phase for SPME–IR, has a better overall optical transparency with useful spectral regions >3035, 2768–1500, 1335–1240, 1204–735 and 710–400 $cm^{-1}$.

### 3.2. Analytes

For the purposes of this study, five organic compounds were chosen that had observable IR bands in PDMS. These compounds, with their major analytical and alternate infrared bands (normalized to the major analytical bands), are shown in Table 1. The major analytical bands are defined as the strongest absorbing bands of the analytes that can be observed in the PDMS solid phase after extracting them into it. It should be noted that all of the compounds have more than one vibrational band

Table 1
Useful analyte bands in poly(dimethylsiloxane)

| Compound | Major analytical band ($cm^{-1}$) | Alternate band ($cm^{-1}$) (% of analytical absorbance band) |
|---|---|---|
| Trifluralin | 1311 | 1548 (80), 1630 (40), 727 (40) |
| *o*-Xylene | 742 | 3019 (11) |
| *p*-Xylene | 1518 | 3022 (16), 3049 (14), 3002 (8) |
| Trichloroethylene | 933 | 962 (40), 947 (16) |
| Perchloroethylene | 911 | NO |

NO, no observable bands.

except perchloroethylene. Additionally, *o*-xylene has the same major analytical band in both PDMS and Parafilm so that a direct comparison between PDMS and Parafilm M at the same wavelength can be performed

It should be noted that when selecting the compounds that can be determined in this film, the optical windows of the PDMS are of major consideration to ensure that the compounds can be observed. That is, at low concentrations, the analyte infrared bands can be masked by the stronger PDMS bands. However, when the analyte concentration is high, its IR bands can often be detected above the PDMS baseline. For example, the upper spectrum in Fig. 2 was obtained of the PDMS film after extracting a 40 ppm solution of *p*-xylene for 60 min. A comparison of this spectrum with the spectrum in Fig. 1 shows that the analyte bands can easily be observed even though the background absorbance is high (e.g., $>1$ AU in the region below 1700 $cm^{-1}$). Additionally, when the analyte concentration is high, the spectrum can easily be identified with the help of a spectral library, as a comparison of the upper and lower spectra in Fig. 2 demonstrates.

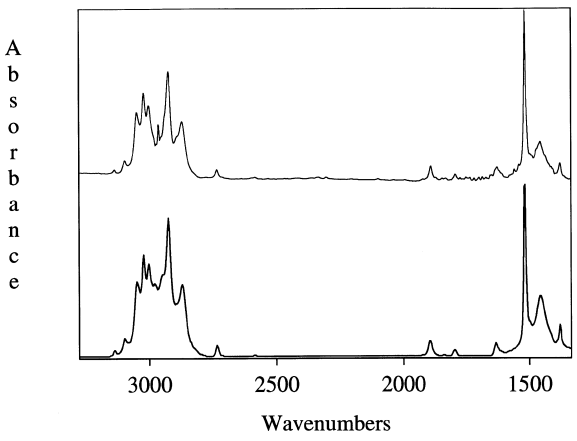


Fig. 2. Infrared spectra comparing SPME–IR results with those from spectral library. Upper spectrum: IR spectrum obtained of the PDMS film after extracting a 40 ppm solution of *p*-xylene for 60 min. Lower spectrum: IR spectrum of *p*-xylene obtained from spectral library. It should be noted that the spectra have been offset for clarity.

### *3.3. Optimum number of scans*

General practice in FT-IR spectrometry involves the co-addition of spectra in order to improve their signal-to-noise ($S/N$) ratios. If the noise is random and the IR signal is constant, then it has been shown that the $S/N$ increases with the square root of the number of scans [12]. However, we showed in previous work that when the compounds are volatile, the increased time needed to co-add scans can also result in a decreased band absorbance due to evaporative loss (i.e., the absorbance signal decreases with respect to time). Since this work employed a different FT-IR spectrometer, we examined the effect of the scan time on detection limit in order to determine if different detection limits were obtained on different instruments. For this study, we chose benzene as a representative volatile analyte.

It was determined that the highest $S/N$ for benzene in PDMS was obtained on this instrument when ca. 25 scans were coadded. This coaddition required 34 s, and is similar to the time frame (within the error of the measurements) required in the previous work employing a different instrument (eight coadded scans requiring 30 s) [5]. Thus, analyte loss due to evaporation from the film (as the spectrum is acquired) appears to be an important factor in governing the detection limit. As a further check of this hypothesis, it was found that the detection limits

Table 2
Equilibration times for selected organic compounds in poly(dimethylsiloxane) and Parafilm M

| Compound | Equilibration time in PDMS (min) | Equilibration time in Parafilm M (min) |
|---|---|---|
| Trifluralin | 75 | NO |
| *o*-Xylene | 80 | 165 |
| *p*-Xylene | 85 | 200 |
| Trichloroethylene | 60 | 300 |
| Perchloroethylene | 60 | 275 |

NO, no observable bands.

of *p*-xylene and *o*-xylene using Parafilm M as the solid phase were similar if obtained on the two different instruments as long as the scan times were similar. However, it should be realized that a $S/N$ improvement of only 1.8× would be expected on increasing the number of coadded scans from eight to 25 and, thus, these results should not be 'over interpreted'. Means of dealing with analyte loss will be the subject of a future communication from this laboratory.

### 3.4. Equilibration times

The times required for the partitioning of the organic compounds between the solid and the aqueous phase were determined by extracting ca. 20–60 ppm aqueous solutions (depending upon the detection limit) for increasingly longer time periods. When the absorbances reached maximum values and remained constant within the relative standard deviations (R.S.D.s) of the measurements, the systems were defined to be at equilibrium.

As shown in Table 2, equilibration times for PDMS range from 60 to 85 min and are faster than those reported by Heglund and Tilotta for Parafilm M [5]. These times are relatively reasonable for analytical measurements, since extractions can be performed in parallel and each spectrum takes less than a minute to obtain. However, the equilibration times were much longer than those reported by Arthur et al. for PDMS films used in the syringe devices [e.g., 2–8 min for benzene, toluene, ethylbenzene and xylenes (BTEX compounds)] [13]. Differences in the equilibration times may be due to differences in the polymer cross-linking of the two phases or to the thicker solid phase used in this work.

### 3.5. Distribution constants

As described in previous work, the distribution constants between the aqueous phase and the PDMS film for the selected compounds were determined optically using their molar absorptivities in $CS_2$ (shown in Table 3) [5]. The resulting constants, along with those obtained with Parafilm and those determined chromatographically, are shown in Table 3. With the exception of trichloroethylene, the $K_d$

Table 3
Molar absorptivity values and distribution constants for selected organic compounds

| Compound | $\epsilon$[a] (l/mm mol) | $\lambda^{-1}$ ($cm^{-1}$) | PDMS | | Parafilm M $K_d$[c] |
|---|---|---|---|---|---|
| | | | $K_d$[b] (this work) | $K_d$ (Lit.) | |
| Trifluralin | 96.8 | 1311 | 794 | NA | NA |
| *o*-Xylene | 36.1 | 742 | 143 | 262[d] | 109 |
| *p*-Xylene | 1.25 | 1888 | 156 | 317[d] | 198 |
| Trichloroethylene | 31.6 | 933 | 8.8 | 1259 | 54.9 |
| Perchloroethylene | 260 | 911 | 24 | NA | 34 |

[a] $\epsilon$ values obtained in $CS_2$ at the wavenumber shown in the following column.
[b] Distribution constant for 127 μm poly(dimethylsiloxane) film.
[c] Distribution constants for 130-μm Parafilm M.
[d] Distribution constants for ca. 100-μm poly(dimethylsiloxane) coatings obtained from Refs [14,15].

Table 4
Calibration curve data for selected organic compounds as determined by SPME–IR

| Compound | Slope (AU/ppm) | Intercept (AU) | $r^2$ | LDR (ppm) |
|---|---|---|---|---|
| Trifluralin | $1.92\times10^{-2}$ | $1.11\times10^{-2}$ | 0.995 | 0.2–2 |
| *o*-Xylene | $3.67\times10^{-3}$ | $5.58\times10^{-2}$ | 0.97 | 5–100 |
| *p*-Xylene | $1.69\times10^{-3}$ | $1.15\times10^{-3}$ | 0.961 | 5–100 |
| Trichloroethylene | $8.75\times10^{-4}$ | $8.16\times10^{-3}$ | 0.992 | 4–100 |
| Perchloroethylene | $4.74\times10^{-3}$ | $2.01\times10^{-4}$ | 0.984 | 1–40 |

values for the various compounds were found to be similar for the PDMS used in this study and Parafilm M. However, it should be noted that significantly larger values were obtained for all compounds for the PDMS used in the syringe device than for the PDMS used in these films. This difference may be due to errors in the assumption in $\epsilon$ (that is, that molar absorptivities of the analytes in $CS_2$ are equivalent to those in PDMS) or in differences in the polymer preparation (i.e., cross-linking) used by the different manufacturing companies.

### *3.6. Calibration information*

Calibration curves for the five analytes were obtained with the SPME–IR method and their equations are shown in Table 4. These curves were obtained at the compounds equilibrium times unless otherwise stated. The linear dynamic range of calibration (LDR) extends from the detection limit (defined here as the quantitation limit) to the largest concentration examined for all analytes. The upper concentration limits were chosen in order to assure that the solutions were not saturated (at least 50 ppm below the solubility limit). The nonzero intercept values are probably due to a slight ratio error between the background and the sample. That is, in standard FT-IR practice the background and sample are normally obtained within a few minutes of each other rather than up to 2 h later and small instrumental drifts may have occurred.

Table 5 lists the detection limits and the relative standard deviations of the measurements along with detection limits in Parafilm M. PDMS detection limits, using the analytical bands shown in Table 1, range from 190 ppb for trifluralin to 4400 ppb for *p*-xylene. PDMS has the lowest detection limits for trifluralin and perchloroethylene. However, the detection limits obtained with PDMS were generally poorer than those obtained with Parafilm because of the significantly higher absorbance of the PDMS spectral background.

Different molar absorptivities ($\epsilon$ values) and distribution constants ($K_d$ values) of the analytes in PDMS explain the significant differences in the detection limits between the analytes studied. These limits follow the general trend that an analyte with a larger $K_d$ and $\epsilon$ will have a better detection limit. This explanation is consistent with the low detection limit of trifluralin and the high detection limit of *p*-xylene.

The R.S.D.s of the determinations for each analyte were obtained by extracting the lowest concentration in their calibration curve. The R.S.D.s are typical for SPME determinations and range from 6.7 to 12%. It should be noted that analyte loss from the film during transfer and FT-IR spectrometric analysis, although significant, does not impair the reproduci-

Table 5
Relative standard deviations and detection limits for the selected organic compounds

| Compound | Concentration (ppm) | Replicate | R.S.D. (%) | Detection limit in PDMS (ppb) | Detection limit in Parafilm (ppb) |
|---|---|---|---|---|---|
| Trifluralin | 0.2 | 3 | 12 | 190 | N/A |
| *o*-Xylene | 5 | 6 | 6.7 | 3060 | 102 |
| *p*-Xylene | 5 | 6 | 8.2 | 4400 | 66 |
| Trichloroethylene | 4 | 6 | 10 | 2700 | 1600 |
| Perchloroethylene | 1 | 6 | 10 | 780 | 1800 |

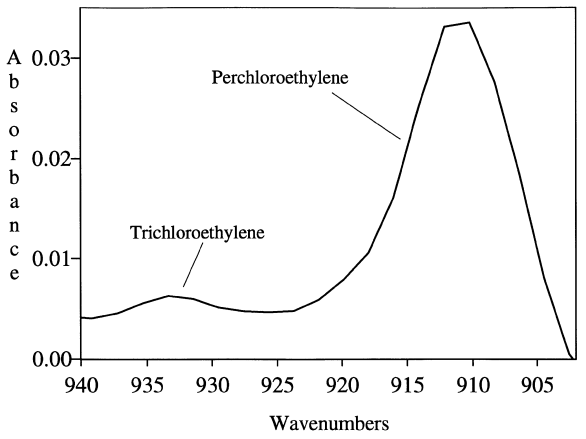


Fig. 3. Infrared spectrum of the 900–940-cm$^{-1}$ region obtained in PDMS following a 60-min extraction of a water sample contaminated with trichloroethylene and perchloroethylene.

bility of this technique as long as the transfer procedures and times are performed as similarly as possible.

### *3.7. PDMS selectivity*

Prior work has shown that the matrix components from real world water samples (e.g. fulvic and humic acids) do not interfere with the partitioning of organic contaminants into the solid phase as long as their concentrations are not too high [3–5]. In order to show the potential selectivity of SPME–IR using PDMS for two similar species, a 2-l sample of lake water was spiked with 5 ppm each of perchloroethylene and trichloroethylene. This solution was allowed to stand at room temperature for 2 days, and then extracted for 60 min with a PDMS film. As shown in Fig. 3, the analytical band of perchloroethylene at 911 cm$^{-1}$ does not overlap the 933 cm$^{-1}$ band for trichloroethylene. Thus, the concentrations of both species can be determined independently.

## 4. Conclusions

PDMS is a useful film for SPME–IR determination of organics in water. For the test compounds examined in this study, PDMS has relatively fast equilibration times (60–85 min) and provides for moderate detection limits (0.2–4.4 ppm).

A comparison between PDMS and Parafilm M shows that extraction of organic compounds by PDMS is faster by about 3-fold. This feature makes PDMS more practical for implementation of SPME–IR as a field analytical method. However, the larger spectral windows of Parafilm M in the IR fingerprint region of 800–1200 cm$^{-1}$ makes it a better film for true unknowns since more spectral information may be obtained. Although the distribution constants are similar for both films, a drawback on the use of PDMS is the higher detection limits for some compounds. However, PDMS does provide for a very low detection limit for trifluralin (190 ppb) which cannot be determined using Parafilm M. Finally, Parafilm M (at US$0.04 per film) is less expensive than PDMS (at US$1.39 per film). However, due to the reusable nature of the films, both are relatively inexpensive.

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