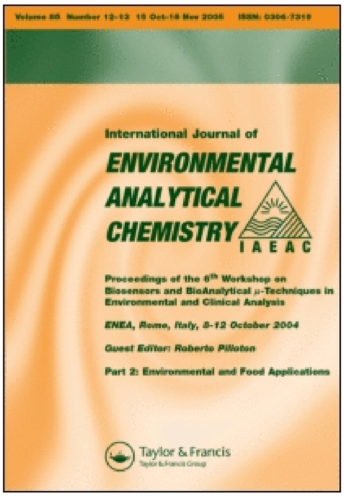

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Flavin, Kevin , Hughes, Helen and McLoughlin, Peter(2007) 'The development of a novel smart mid-infrared sensing methodology for residual solvents', International Journal of Environmental Analytical Chemistry, 87: 1, 29 — 42

To link to this Article: DOI: 10.1080/03067310600833443
URL: http://dx.doi.org/10.1080/03067310600833443

Intern. J. Environ. Anal. Chem.
Vol. 87, No. 1, 15 January 2007, 29–42

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The development of a novel smart mid-infrared sensing methodology for residual solvents

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(*Received 1 February 2006; in final form 8 May 2006*)

The potential of a novel polymer modified mid-infrared technique as a ‘smart’ sensing methodology is demonstrated. Diffusion of a penetrant (analyte molecule) was monitored into a Teflon® AF2400 membrane through observation of one of its infrared absorption bands. During the diffusion of select analytes, mid-IR polymer bands were observed to experience a red shift (reduction in absorption frequency). The rate of appearance of these bands matched that of analyte diffusion. As these bands are specific to certain analytes, and their intensity is analyte-dependent, monitoring of these shifted bands forms the basis of a ‘smart’ sensing regime. The suitability of this smart sensing methodology for the enhanced detection of several residual solvents is presented. A fivefold increase in sensitivity through the monitoring of these bands was realized for the detection of ethylbenzene. One of the aims of this work was to determine whether the cause of the polymer band shifting is chemical or optical in nature. Result data presented support the hypothesis that polymer/diffusant interactions cause this band shifting. This is demonstrated by the fact that a penetrant (tetrahydrofuran), which affected a band shift in the polymer, displayed a blue shift (increase in absorption frequency) in its own spectrum. Ethanol did not cause a polymer band shift and displayed no band shifts in its absorbance spectrum. The relative absorbance of the shifted polymer bands is compared between analytes and does not demonstrate a correlation to analyte refractive indices supporting a polymer/diffusant interaction hypothesis.

Keywords: Teflon® AF2400; Mid-infrared spectroscopy; Total attenuated reflectance; Polymer interactions; Pre-concentration

1. Introduction

Smart or intelligent materials are those which respond to changes in their environment. Stimuli-responsive polymers are one category of these materials. There are various stimuli, which may be classified as either chemical or physical [1]. Ionic strength [2], pH [3, 4], and chemical agents [5] are chemical stimuli, which cause a change in interactions between polymer chains or between polymer chains and solvents at the molecular level. Temperature [6], light [7], electric [8], or magnetic [9] fields and mechanical stress are physical stimuli and will affect the level of energy sources and alter molecular interactions at critical onset points.

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International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online
DOI: 10.1080/03067310600833443

Smart sensors are those in which the physical or chemical properties within the sensor/material are altered by the presence of an analyte. The response to the stimuli may be measured and quantified as opposed to direct measurement of an analyte property. Smart sensors based on polymeric chemoresistors (conducting polymer resistors) for the detection of vapours/odours have been reported [10, 11]. The most commonly used principle for such sensors is one in which a change in the sensor resistance ΔR_S is monitored during exposure to a gas. The selective detection of analytes using indicator dyes is described [12–15], where the dyes may be embedded in various polymeric materials and undergo reversible chemical reactions with the analyte, resulting in changes in absorbance or fluorescence. Analytes may also be selectively pre-concentrated through molecularly imprinted polymers [16, 17]. If the molecularly imprinted polymer displays transparency, analytes may be quantified by changes in their absorbance/fluorescence [18, 19]. Another approach is to trap or graft components within the polymer, which react in the presence of the template [20, 21]. Quantum dots have been used which exhibit photoluminescence in the presence of template molecules [21].

The use of polymer-modified ATR-FTIR spectroscopy is a well-established methodology for the determination of residual solvents [22–26]. This sensing methodology utilizes a wave-guide, usually a crystal [22, 23, 27] or fibre [24–26, 28] coated with a polymeric material with the aim of pre-concentrating predominately non-polar components from an aqueous matrix. Pre-concentration occurs as a result of an analyte partitioning between the aqueous and polymeric phases. As the mid-IR beam undergoes attenuated total reflection (ATR) within the wave-guide a standing evanescent wave occurs at the point of internal reflection. The magnitude of this wave is measured by the depth of penetration (d_p) illustrated in equation (1), which is a function of the angle of incidence of the light beam (θ), refractive index of both the surrounding medium (n_s), the wave-guide (n_c), and the wavelength of light absorbed (λ) [29]:

$$d_p = \frac{\lambda}{2\pi n_c \sqrt{\left(\sin^2\theta - (n_s/n_c)^2\right)}}. \tag{1}$$

The polymer film is frequently coated to approximately three times the depth of penetration, which is considered the entire sensing region as the evanescent field has decayed to 5% of its original value [30]. As well as pre-concentration of analytes, the hydrophobic membrane ensures the exclusion of interfering water from within this region.

As the analyte is absorbed into the polymer, it enters the evanescent sensing region. In order to analytically assess penetrant behaviour during diffusion into the polymer, experimental data are fitted to a mathematical model derived by Fieldson and Barbari [31]. The model is based on Fick's second law, an expression for transient Fickian diffusion, and is used to characterize penetrant diffusion by estimation of a diffusion coefficient (D) and equilibrium absorbance (A_∞). Initially, a diffusion curve is simulated based on wave-guide and polymer refractive indices, polymer membrane thickness, and band wavelength. A_∞ is hence calculated followed by estimation of D based on best fit to the experimental data. The use of a predictive modelling approach based on the Fickian model has resulted in reduced sensing times using this polymer-modified sensing approach [32].

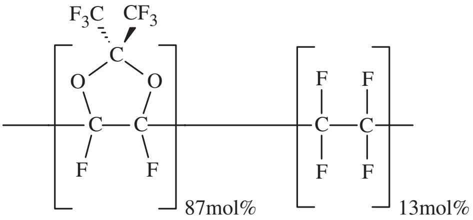

Figure 1. Repeat unit of Teflon® AF2400 a copolymer of 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE) [33].

The cladding material under investigation in this work is a copolymer of 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE) commercially known as Teflon® AF2400, where the PDD content is 87 mol% (figure 1) [33]. It is the extensive dioxole content within the polymer resulting in disruption of polymer chain packing, which makes it an amorphous polymer. Its amorphous nature results in a high fractional free volume (FFV) of 0.327 [34] allowing high analyte uptake and rate of permeation [34, 35], necessary for good pre-concentration. Teflon® AF2400 has considerable optical transparency, which makes it suitable as a mid-IR sensor component. Its perfluorinated nature results in elevated thermal stability with a glass transition temperature (T_g) of 240°C [33], the benefit of no C–H stretching absorbencies (figure 2) and exceptional chemical resistance. Teflon® AF2400 is only soluble in a number of perfluorinated solvents and hence is not affected by dissolution as pre-concentration of solvent penetrants occurs. The above-mentioned properties of Teflon® AF2400 including optical transparency, high free volume, and robustness result in a polymer uniquely suitable as a pre-concentrating medium for this technique [22, 36]. Figure 2 illustrates a mid-infrared ATR spectrum of Teflon® AF2400 with the main absorbance bands indicated. The bands at 1142, 1204, and 1239 cm^{-1} are stretching vibrations due to CF_2 and CF_3 units [37]. 1094 and 986 cm^{-1} may be attributed to the cyclic ether linkages [29].

Unexpected shifted polymer infrared bands have been observed during the diffusion of particular analytes into Teflon® AF2400 [23]. These altered bands correspond to the seven Teflon® AF2400 absorbance bands indicated in figure 2. Murphy *et al.* previously predicted two possible causes of the alteration of the bands, one of which is chemical and the other optical in nature [23]. This is only the second publication discussing the analyte-specific effect within Teflon® AF2400 when used as a cladding material for optical sensing. The purpose of this paper is to investigate whether the origin of these bands is chemical or physical in nature, to discuss the potential use of this polymer band shifting ‘effect’ as a novel smart sensing technique, and to determine whether enhanced sensitivity can be achieved through the monitoring of such bands.

2. Experimental

2.1 *Materials*

Teflon® AF2400 fluoropolymer was obtained as a 1% solution in FC-75 perfluorinated solvent from DuPont (Wilmington, DE). Absolute ethanol was obtained at 99.5% (v/v)

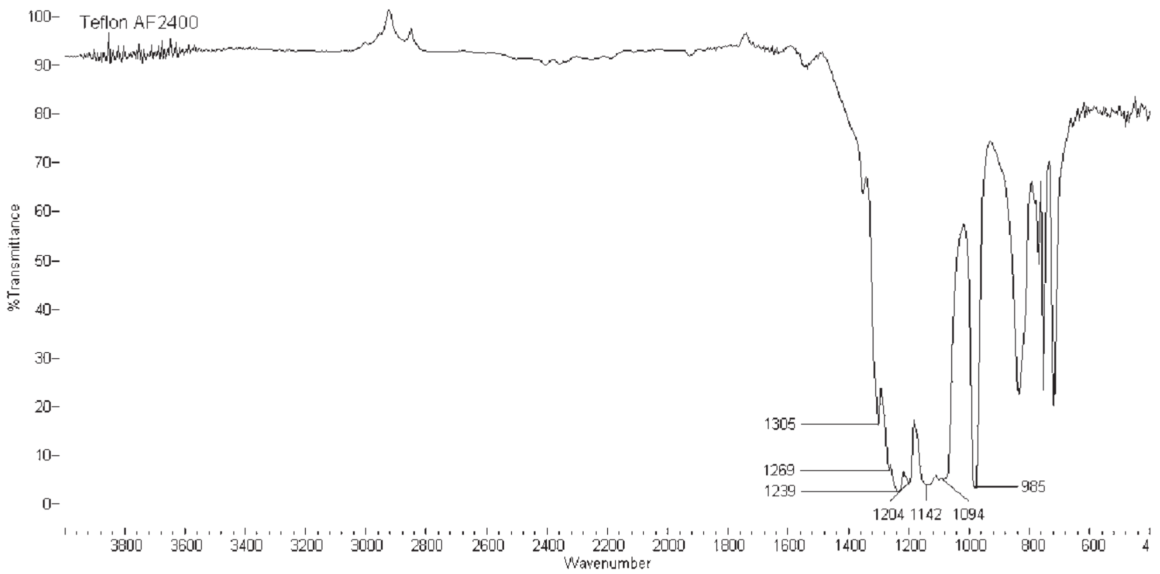

Figure 2. Mid-infrared ATR spectrum (20 co-scans) of Teflon® AF2400 with the major bands indicated at a resolution of $4\,\mathrm{cm}^{-1}$.

purity from Merck. Both toluene and tetrahydrofuran were obtained at 99.9% purity from Romel Ltd. Ethylbenzene was obtained at 99% purity from BHD Chemical Ltd. The xylene isomers were purchased from Lancaster at 99% purity.

2.2 *Experimental*

A BIO-RAD Excalibur series 3000 FTIR spectrometer equipped with a cryogenic mercury cadmium telluride (MCT) detector was used for measurements. The wave-guide was a trapezoidal ZnSe crystal (MacroOptica Ltd., Moscow) with dimensions of 72 mm × 10 mm × 6 mm and a 45° angle of incidence giving six reflections in contact with the sample.

Teflon® AF2400 was coated onto the wave-guide using a Chemat Technology KW-4A spin coater. The spectral range of significance in this investigation is from 3033 to 878 cm^{-1}, where d_p is at a maximum of 1.64 µm at 878 cm^{-1}. The Teflon AF2400 was coated to a thickness of 5.1 µm, which is approximately three times the maximum d_p utilized for measurement. The polymer film was cured at 25°C for 10 min, 112°C for 10 min, 245°C for 5 min, and 330°C for 10 min.

The coated crystal was fitted into a Specac Thermostabilized Top Plate stainless steel temperature-controlled ATR flow cell (110 µL). Analyte solutions were pumped over the surface of each polymer at 5 $\mathrm{mL\,min}^{-1}$ using a Shimadzu LC-10ATvp solvent delivery system. Analyte solutions were temperature-controlled during analysis using a Grant W20 thermostabilized water bath. When preparing solutions, all analytes were measured directly into low-headspace volumetric glassware and dissolved with sonication prior to use. Fresh solutions were prepared for each run. Measurements of pure solvents were taken over a Specac ATR trough cell. All experiments were carried out in triplicate, and all solutions were sealed during analysis.

3. Results and discussion

3.1 *Origin of red-shifted polymer bands*

As specific analytes diffuse into Teflon® AF2400, a set of infrared bands appear which are not indicative of those analytes. An example of the appearance of these bands was observed during the diffusion of ethylbenzene into a Teflon® AF2400 film. The bands are illustrated in figure 3 overlaid on Teflon® AF2400 absorption bands between 1305 and 986 cm^{-1}. The red shifted bands correlate to the Teflon® AF2400 absorption bands.

The diffusion profile of an ethylbenzene C–H stretch (2973 cm^{-1}) and two of the shifted polymer bands (1302 and 978 cm^{-1}) are illustrated in figure 4. Each of the averaged experimental data sets is correlated to its best-fit simulated data set. These bands are observed to appear at the same rate as the penetrant and demonstrate an amplified response. On normalization of the penetrant and shifted polymer diffusion profiles, they become nearly identical [23] substantiating the affiliation between the penetrant and the shifted bands. The diffusion profile of ethylbenzene is observed to be Fickian in nature as it displays a good fit to the theoretical model. Both effect bands selected also display excellent fits to the model, indicating further evidence of a

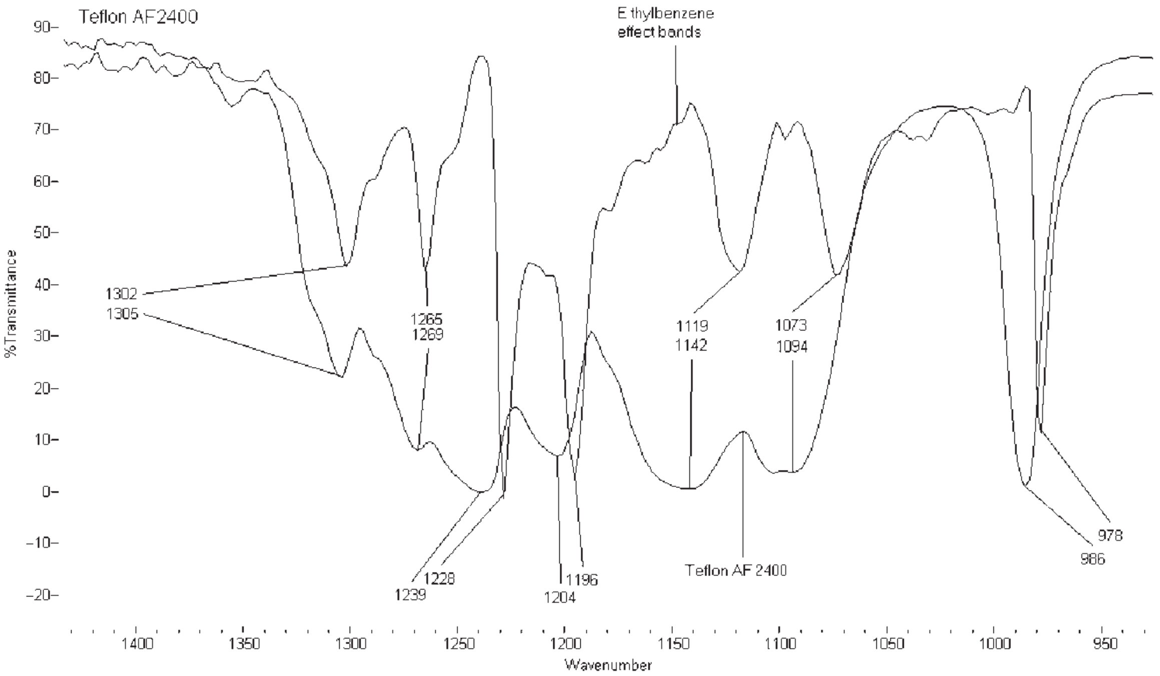

Figure 3. Spectrum (20 co-scans) of a 5.1 μm Teflon® AF2400 film (lower spectrum) overlaid on 'effect' bands observed during 100 ppm ethylbenzene diffusion into the same film at 25°C after 20 min (upper spectrum), both with a spectral resolution of $4\,cm^{-1}$.

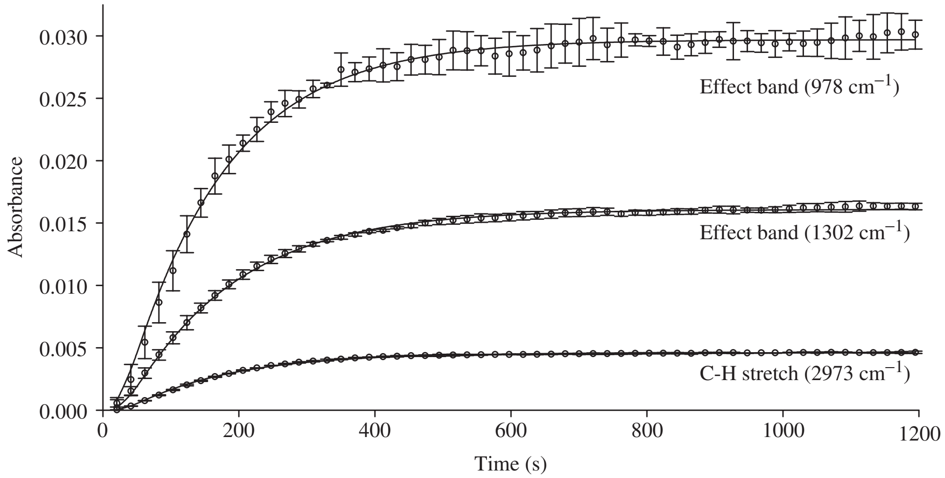

Figure 4. Ethylbenzene diffusion (100 ppm) into a 5.1 µm Teflon® AF2400 film based on triplicate analysis with 95% confidence intervals. All diffusion data were obtained utilizing a water-saturated polymer as a background. The aliphatic C–H stretch and two of the 'effect' bands are fitted to a theoretical Fickian model [29] displayed by the best-fit curves.

correlation between penetrant diffusion and the shifted polymer bands. The diffusion coefficients (D) for the bands in figure 4 are as follows: C–H stretch (2973 cm^{-1}) $D = 7.61 \pm 0.11 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$; 'effect' band (1302 cm^{-1}) $D = 7.28 \pm 0.14 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$; 'effect' band (997 cm^{-1}) $D = 7.47 \pm 0.15 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$. The D values are within error, which reiterates the relationship between analyte diffusion and the appearance of the shifted polymer bands. D values estimated for the shifted polymer bands were equal to that of the diffusing analyte in all cases.

The influence of penetrant concentration on the shifted polymer bands has been demonstrated [23]. In order to reveal the enhancement of sensitivity possible through monitoring of the shifted bands, limits of detection (LOD) for toluene and ethylbenzene were calculated from their characteristic absorptions. These values are 27 and 24 µL L^{-1}, respectively. LOD values of 13 and 5 µL L^{-1} for toluene and ethylbenzene, respectively, were calculated using the shifted polymer band at 1302 cm^{-1}. The LOD values demonstrated substantial enhancement of the sensitivity of the method, with ethylbenzene displaying a fivefold sensitivity increase resulting from the utilization of the band at 1302 cm^{-1}. Figure 5 illustrates concentrations for toluene and ethylbenzene at which the analyte shifted polymer bands are present, and the characteristic analyte bands are still below their detection limits. The use of optical fibres in which many more internal reflections are possible can result in further sensitivity increases of orders of magnitude over ATR systems [38, 39].

3.2 *Chemical or physical effect?*

There are two proposed mechanisms for the occurrence of this polymer band shifting. The first is chemical, where the penetrant interacts with the polymer and in doing so causes a change in the infrared absorbance of the polymer. Examples of such interactions are hydrogen bonding, dipole, or π–π interactions [40]. The second

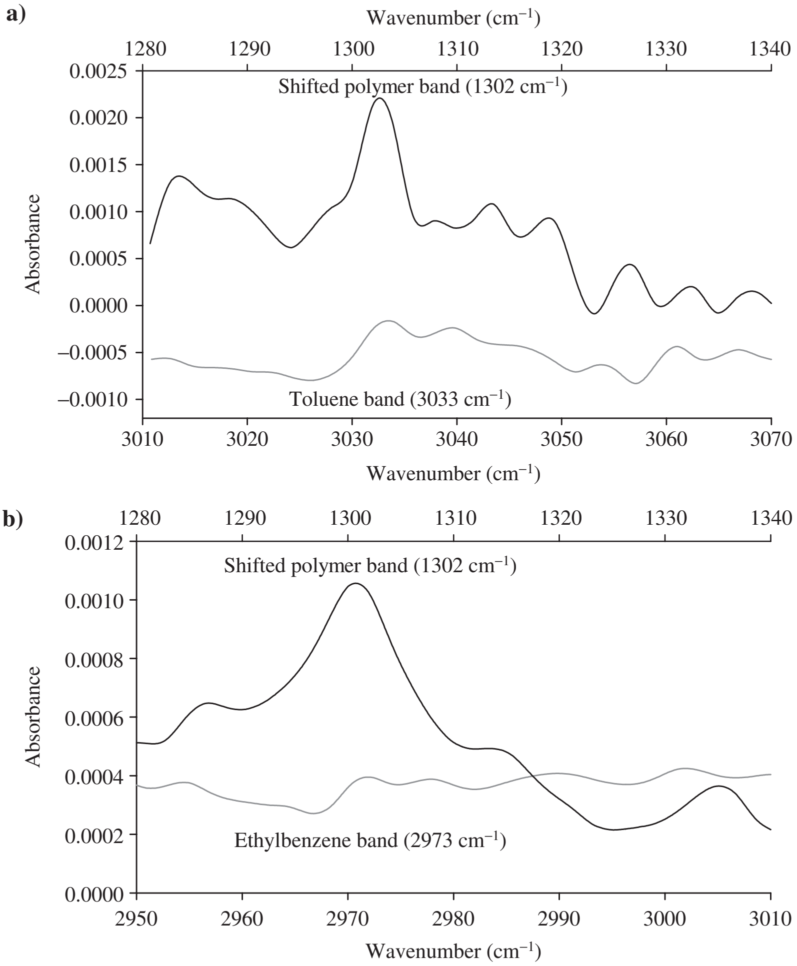

Figure 5. (a) Toluene ($20\,\mu\mathrm{L\,L^{-1}}$) diffusion into a 5.1 μm Teflon® AF2400 film; aromatic C–H (3033 cm^{-1}), toluene-shifted polymer band (1302 cm^{-1}). (b) Ethylbenzene ($5\,\mu\mathrm{L\,L^{-1}}$) diffusion into a 5.1 μm Teflon® AF2400 film; aliphatic C–H (3033 cm^{-1}), toluene-shifted polymer band (1302 cm^{-1}).

possibility is a physical effect, in this case optical. Equation (1) illustrates the dependence of d_p on the refractive index of the polymer. If this were to change significantly during penetrant diffusion into the polymer, it would result in alteration of the evanescent field magnitude. The refractive indexes of Teflon® AF2400 and ethylbenzene are 1.29 of 1.49, respectively. Any change in the membrane refractive index, which may occur, would certainly be an increase as Teflon® AF2400 does not demonstrate plasticization [41]. This corresponds to an expansion of the evanescent field and an increase in the quantity of polymer within the sensing region resulting in the formation of positive polymer absorption bands.

A list of all penetrants monitored into Teflon® AF2400 followed by their refractive indices are illustrated in table 1. Analytes are displayed in two groups, those in which shifted polymer bands are present and those in which they are absent. All analytes, which cause the appearance of shifted polymer bands, exhibit refractive indices of 1.407

Table 1. Analytes monitored into Teflon® AF2400 followed by their refractive index values.

'Effect' bands present		'Effect' bands absent	
Analyte	Refractive index	Analyte	Refractive index
Toluene	1.499	Methanol	1.329
Ethylbenzene	1.493	Ethanol	1.362
1,2-Xylene	1.495	1-Propanol	1.384
1,3-Xylene	1.503	2-Propanol	1.377
1,4-Xylene	1.496	Acetone	1.359
Chlorobenzene	1.524	*n*-Pentane	1.358
1,2-Dichlorobenzene	1.551	Water	1.333
1,2,4-Trichlorobenzene	1.571		
Flourobenzene	1.466		
1,1-Dichloroethane	1.425		
Trichloroethane	1.476		
Tetrachloroethane	1.506		
1-Chloropentane	1.412		
Chlorocyclopentane	1.451		
Tetrahydrofuran	1.407		

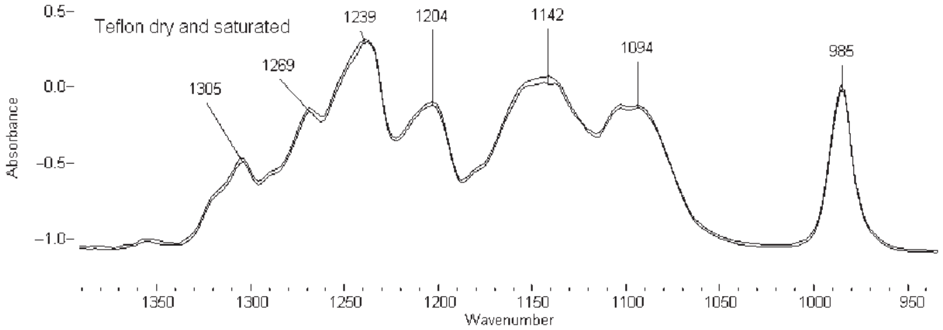

Figure 6. Teflon® AF2400 membrane (5.1 μm) before and after saturation with water.

(tetrahydrofuran) or greater. In concurrence, all analytes which do not cause the appearance of shifted polymer bands exhibit refractive indices smaller than that of tetrahydrofuran. On this evidence alone, the effect seems purely optical in nature, where penetrants of higher refractive index provide a large enough change in the membrane refractive index to cause the appearance of the shifted polymer bands.

A simple refractive index change, however, does not explain frequency shifts displayed by the effect bands. A sample background was taken of the polymer-modified ATR crystal prior to monitoring sample pre-concentration. In this instance, a background was taken preceding the coating of the polymer to the wave-guide. This allowed the observation of Teflon® AF2400 absorption bands during the saturation of the membrane with water from dry. Figure 6 displays the polymer before and after its saturation with water, indicating no polymer band shifts. It is evident from this result that the polymer bands were not simply shifted due to molecular association with water. Sammon *et al*. demonstrated polymer band shifts in polyethersulphone (PES) [42, 43] as a result of water absorption.

Various authors have discussed polymer absorbance band shifting as a result of molecular interactions [44–46]. Moskala *et al*. found that the carbonyl group of poly (vinyl acetate) red shifted by 16 cm^{-1} on addition to a blend with poly(vinyl phenol) as a result of hydrogen bonding with the hydroxyl group. The carbonyl band intensity also increased as the poly(vinyl phenol) content of the blend increased [44]. This may be analogous to the band shifts incurred by Teflon® AF2400 on addition of an effect causing analyte followed by increased absorbencies of the shifted bands with increasing analyte concentration. Maillo *et al*. studied the interaction between fibre of polyamide 6 and iodine. It is observed that treatment of the polyamide with iodine results in an N–H band blue shift of 100 cm^{-1}. There is also a decrease in the shifted N–H band absorbance as a result of breaking of hydrogen bridges by the iodine [45]. Both the direction of the band shift and the absorbance change are opposite to those observed in Teflon® AF2400, which substantiates that interactions are being formed between the penetrant and the polymer. Coleman *et al*. found that the carbonyl absorption band of poly(ε-caprolactone) shifted to lower frequencies on addition to blends with poly(vinylchloride) as a result of inter-polymer hydrogen bonding [46].

The C–H stretching bands of toluene, ethylbenzene, tetrahydrofuran, ethanol, and the xylene isomers experience frequency blue shifts during pre-concentration within the polymer (table 2). Similar increases in C–H stretching frequencies have been observed for acetone [47], poly(*N*-isopropylacrylamide) [48] and poly(methoxyethylacrylate) [49] in the presence of water. The band shifts may be attributed to the electronic redistribution in the C–H bonds concurrent with the change in the polarization of the surrounding water molecules. Teflon® AF2400 absorbs water to a small extent, and all analytes are pre-concentrated from aqueous solution. The presence of water may be the source of the C–H band shifts in each of the penetrants.

The band shifts of two analytes were monitored in order to determine whether further analyte band shifts were the result of an aqueous environment or possible interactions with the polymer. Tetrahydrofuran was monitored as it has a high enough water solubility to be monitored directly in aqueous solution, in addition to causing polymer shifted band formation. Ethanol was utilized as it may also be directly monitored, but it does not produce the effect. In the case of ethanol, in addition to the methyl C–H stretch at 2972 cm^{-1}, two C–O stretches are displayed in table 3 at 1045 and 880 cm^{-1} [40]. Neither of the C–O stretches is shifted in aqueous solution or during pre-concentration within Teflon® AF2400. This demonstrates a lack of molecular interactions between ethanol and Teflon® AF2400 and would agree with an interaction hypothesis as the ethanol does not cause the effect. The THF C–O–C stretches at 1066 and 908 cm^{-1} were shifted to lower frequencies when in aqueous solution (table 3). This occurs due to hydrogen-bonding interactions, where acceptor group stretching absorptions are shifted to lower frequencies [40]. The 1066 and 908 cm^{-1} bands are shifted to higher frequencies when absorbed into Teflon® AF2400. This illustrates that

Table 2. Analyte C–H absorbance frequencies (cm^{-1}) neat and in Teflon AF2400 at a resolution of 4 cm^{-1} (20 scans).

Analyte	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene	THF	Ethanol
Neat	3026	2964	2940	2920	2921	2857	2972
In Teflon	3033	2973	2945	2929	2932	2870	2983

Table 3. THF and ethanol absorbance frequencies (cm^{-1}) neat, in water and in Teflon AF2400.

Analyte	THF				Ethanol		
Neat	2973	2857	1066	908	2972	1045	880
In water	x	2885	1041	885	2982	1045	878
In Teflon	2983	2870	1070	918	2983	1045	879

Table 4. ATR-FTIR triplicate measurements of neat polymer band shift causing analytes of concentration (C); refractive index (n_{25}), absorbance (A) with 95% confidence intervals (CI) at wavelength (λ)[a].

	A	95% CI	n_{25}	λ (cm^{-1})	$3 \times d_p \times 104$ (cm)	C ($mol\,L^{-1}$)	ε	A_∞	95% CI	C_p ($mol\,L^{-1}$)
Toluene	0.1411	0.00028	1.499	3033	1.428	9.35	229	0.0013	0.00007	0.120
Ethylbenzene	0.2739	0.00074	1.493	2973	1.456	8.13	508	0.0046	0.00003	0.187
m-Xylene	0.2019	0.00099	1.495	2929	1.478	8.10	367	0.0033	0.00011	0.182
o-Xylene	0.1715	0.00007	1.503	2945	1.470	8.25	303	0.0032	0.00013	0.214
p-Xylene	0.2328	0.00007	1.496	2932	1.477	8.06	425	0.0046	0.00035	0.218
THF	0.4328	0.00157	1.410	2983	1.452	12.33	522	0.0031	0.00011	0.123

[a] Path length was taken as three times d_p and concentration calculated from analyte density. Average equilibrium absorbance (A_∞) values of 'effect' causing analytes diffusing into Teflon® AF2400 also based on triplicate runs with 95% confidence intervals. A_∞ and extinction coefficient (ε) values were used to calculate analyte concentration within the polymer (C_p).

the THF is no longer interacting with the water but is interacting with the polymer in an alternative manner. The shifts demonstrated by THF also agree with an interaction hypothesis, as they provide evidence of interaction between THF and Teflon® AF2400.

3.3 *'Effect' band magnitude*

The extent to which the 'effect' occurs within the polymer may be compared between analytes. However, simply comparing the absorbance of a specified shifted polymer band for two analytes of equal concentration is not possible, for two reasons. First, as a result of the variation in analyte partition coefficients between their aqueous matrix and the polymer, equal analyte solution concentrations shall not result in equal analyte concentrations within the polymer. Second, variation of molar extinction coefficients between analytes makes them directly incomparable. To effectively compare the 'effect' between analytes, molar extinction coefficients must be calculated, followed by the analyte concentration within the polymer.

The molar extinction coefficient of each analyte was calculated using the Beer–Lambert law [50] from an ATR measurement of the pure analyte, where the path length was taken to be three times d_p and the analyte concentration (C) calculated from its density (table 4):

$$\varepsilon = \frac{A}{3d_pC_s}, \tag{2}$$

where the molar extinction coefficient (ε) is a function of the analyte absorbance (A), the path length ($3d_p$) and the analyte solution concentration (C_s). The d_p for each analyte was calculated using the wavelength of the analyte absorption band and the refractive index of the pure analyte (equation (2)).

Table 5. Shifted polymer band absorbance (A_e) is measured at $1302\,cm^{-1}$; the analyte concentration within the polymer (C_p); the relative 'effect' (R_e) and the analyte concentration in solution (C_s).

	A_e	95% C.I.	C_p (mol L^{-1})	R_e (mol dm^{-3})	C_s (mol dm^{-3})
Toluene	0.0063	0.00031	0.120	0.0525	0.00094
Ethylbenzene	0.0161	0.00021	0.187	0.0862	0.00081
m-Xylene	0.0138	0.00043	0.182	0.0759	0.00081
o-Xylene	0.0163	0.00053	0.214	0.0762	0.00083
p-Xylene	0.0184	0.00115	0.218	0.0842	0.00081
THF	0.0034	0.00041	0.123	0.0277	0.24653

The molar extinction coefficient (ε) (table 4) was subsequently employed to determine the analyte concentration within the Teflon AF2400 membrane (C_p) in table 4. The assumption is made that the alteration of the refractive index (n), and hence d_p, is negligible during analyte permeation. d_p was thus calculated for each analyte using the Teflon® AF2400 refractive index (1.29) at its absorption wavelength within the polymer. In order to validate the calculated C_p values, partition coefficients between Teflon® AF2400 and water were calculated and compared with log $K_{o/w}$ values, for all analytes utilized, from the literature [51]. A linear correlation is demonstrated between the two sets of values displaying an r^2 value of 0.995.

The relative 'effect' (R_e) in table 5 is determined from the shifted polymer band absorbance (A_e) at $1302\,cm^{-1}$ and the analyte concentration within the polymer (C_p) (table 5). R_e is the absorbance of the shifted polymer band at $1302\,cm^{-1}$ for a 1 molar analyte concentration within the polymer. This allows a comparison of the magnitude of this phenomenon between analytes. If the hypothesis was correct that a change in refractive index due to absorption of the analyte caused the appearance of shifted polymer bands, a molar solution of analyte with a higher refractive index should result in a larger shifted polymer band absorbance. Toluene has a larger refractive index than ethylbenzene, meta- and para-xylene (table 4). However, all three display a larger relative effect than toluene again supporting a polymer/analyte interaction hypothesis. This also occurs where ethylbenzene has a smaller refractive index than both *meta*- and *ortho*-xylene but demonstrates a larger relative effect.

4. Conclusion

Polymer band shifting during the diffusion of specific molecular species into Teflon® AF2400 was observed. It was revealed that band shifting is directly related to the absorption by the polymer of certain penetrants. Diffusion and concentration profiles of these bands all followed that of the penetrant closely. As the bands display amplification of penetrant absorption bands, they may be employed as a means of increasing sensitivity (e.g. a fivefold increase in sensitivity was observed for ethylbenzene as a result of the shifted polymer band at $1302\,cm^{-1}$). As a result of the analyte specificity of the 'effect', analytes with interfering absorption spectra may be analysed in the presence of one another.

The evidence in favour of an optical 'effect' is that all penetrants with higher refractive index values than tetrahydrofuran cause the appearance of the shifted polymer bands, and all penetrants with refractive index values below it do not. Frequency shifts of these bands make it more likely a result of a molecular interaction with the polymer. It was revealed that these band shifts were not as a result of interaction between water and the polymer, which only leaves the possibility of interaction between the penetrant and polymer. An effect-causing penetrant (THF) displayed absorbance band shifts in its spectrum, where a non-effect-causing penetrant (ethanol) did not. A novel method for the calculation of analyte concentrations within the pre-concentrating medium was demonstrated. This method was used to access the magnitude of the ‘effect’ among analytes. If the ‘effect’ was a result of refractive index variation, an analyte of higher refractive index should display a greater relative ‘effect’. As the relative ‘effect’ caused by toluene (higher *n*) was less significant than the molar ‘effect’ caused by ethylbenzene (lower *n*), a breakdown of the optical hypothesis occurs. Through a combination of observations, the cause of the analyte specific ‘effect’ within Teflon® AF2400 was determined to be interactions between penetrant (analyte) molecules and the polymer. This novel ‘smart’ sensing methodology demonstrates a clear advantage over traditional pre-concentrating methods as a consequence of both enhanced sensitivity and its selective analyte response.

Acknowledgements

We wish to thank Merck, Sharpe & Dohme, Ballydine, Co. Tipperary, Ireland and Enterprise Ireland for funding under the Innovation Partnership programme. We wish to acknowledge DuPont for the provision of Teflon® AF2400 fluoropolymer, Chestnut Run Plaza, 705/GS38, Wilmington, DE 19880-0705, USA.

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