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MEASUREMENT OF THE RATES OF DIFFUSION OF HALOMETHANES INTO POLYMER FILMS USING ATR-FTIR SPECTROSCOPY

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Polymer-modified attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and FEWS (fibre-optic evanescent wave) spectroscopy have been very successful to date for sensitive detection of organic pollutants in water utilising the mid-infrared (MIR) region of the electromagnetic spectrum ($4000\text{--}400\text{ cm}^{-1}$). This sensing approach involves the use of different polymer films for preconcentration with optimisation of the sensor related to the rate of diffusion of solvent molecules into these polymer films. Compounds such as chloroform, bromoform, bromodichloromethane and dibromochloromethane which are collectively referred to as trihalomethanes (THMs) were analysed in this work. A gaseous phase experimental design was used and from experimental data the rate of diffusion of each of the halomethanes was quantified based on a Fickian type diffusion model. Individual diffusion coefficient values were found to be in the range $3.38\text{ E-}10 \pm 0.01\text{ E-}10$ to $4.72\text{ E-}08 \pm 0.42\text{ E-}08\text{ cm}^2\text{ s}^{-1}$. Multicomponent effects were observed for mixtures of compounds diffusing into polyisobutylene and ethylene-propylene copolymer.

Keywords: Polymer films; ATR-FTIR spectroscopy; Polyisobutylene; Ethylene-propylene copolymer; Halomethanes; Diffusion

INTRODUCTION

The increasing demands of national and European directives concerning the environmental protection of resources are having a significant impact on the development of advanced sensors. There is an increasing need for more detailed information concerning the presence and quantity of chemical species such as pesticides and other chlorinated hydrocarbons in the environment. There is also a need to develop sensors that can provide this information on-line from the point of intake and discharge [1]. Contaminants need to be both identified and quantified as rapidly as possible. Current techniques for volatile organic chemical quantitation include headspace gas chromatography. However, such techniques are not suited to rapid *in situ*, online measurements.

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The advantages of optical bulk membrane sensors for the detection of chemical species have been highlighted by Spichiger [2].

For air monitoring purposes the properties of solubility, vapour pressure, and molar volume can be applied to select an analyte collection procedure and also to study the rates of diffusion of these analytes into polymer films [3].

Halogenated hydrocarbons, especially chlorine derivatives, pose a serious threat to the environment, as many are toxic or even carcinogenic. Their presence in the environment is widespread and from a variety of sources, namely industrial and domestic waste. Chlorinated hydrocarbons may also be produced during the disinfection of drinking water [4].

Organohalides are formed through the reaction between chlorine and organic matter in water. These organohalides include the trihalomethanes (THMs). Species such as chloroform (CHCl_3), bromoform (CHBr_3), bromodichloromethane (CHBrCl_2), and dibromochloromethane (CHBr_2Cl) are collectively termed as total THMs (TTHMs). The US Environmental Protection Agency (USEPA) has adopted a MCL (maximum contaminant level) value of $80 \mu\text{g L}^{-1}$ for TTHMs in ground and drinking water [5]. The World Health Organisation (WHO) has set guideline values of 200, 60, 100, and $100 \mu\text{g L}^{-1}$ in drinking water for CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3 , respectively [6].

A technique that has been very successful to data for the sensitive detection of organohalide analytes in both the aqueous and gaseous phases is polymer-modified attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy [4,7]. In ATR spectroscopy, a beam of radiation passes through an interface between two materials of different refractive indices. Although the beam is totally reflected at the interface, radiation does penetrate a small distance into the medium of lower refractive index. This penetrating radiation is called the evanescent wave. If the less dense medium is capable of absorbing the IR radiation, the reflected beam is attenuated at characteristic wavelengths corresponding to the absorption bands of the less dense medium. This is known as attenuated total reflection. In ATR spectroscopy, the sample is placed tightly against the surface of a prism or an internal reflection element. With the appropriate incident angle, the IR beam undergoes multiple internal reflections before it passes out of the ATR crystal. Attenuation due to absorption can take place at each reflection.

A typical ATR crystal with a polymer cladding is shown in Fig. 1.

The sensitivity of an ATR sensor can be greatly enhanced by coating the internal reflection element (IRE) with a thin layer of a polymer (see Fig. 1). The polymeric layer extracts the analyte from the bulk phase, thereby increasing the effective concentration of the analyte within the penetration depth of the evanescent wave. It has been shown that if a diffusing molecule has an affinity for the polymeric phase, detection limits for ATR spectroscopy can be improved due to this preconcentration of the analyte [7]. Silver halide fibres have also been used as IREs to increase the number of internal reflections and therefore increase sensitivity [8].

Göbel *et al.* [8] investigated the use of ethylene-propylene copolymer (E-Pco) (% E-P monomers not specified) and polyisobutylene PIB in the detection of aqueous solutions of chloroform using ATR-FTIR spectroscopy. The system incorporated a ZnSe crystal within a flow cell. Homogenous 3% (w/w) polymer films of between 10 and $40 \mu\text{m}$ ($\pm 2 \mu\text{m}$) were used, at room temperature (exact temperature not specified). Theoretical models of the diffusion processes were simulated for both stopped-flow

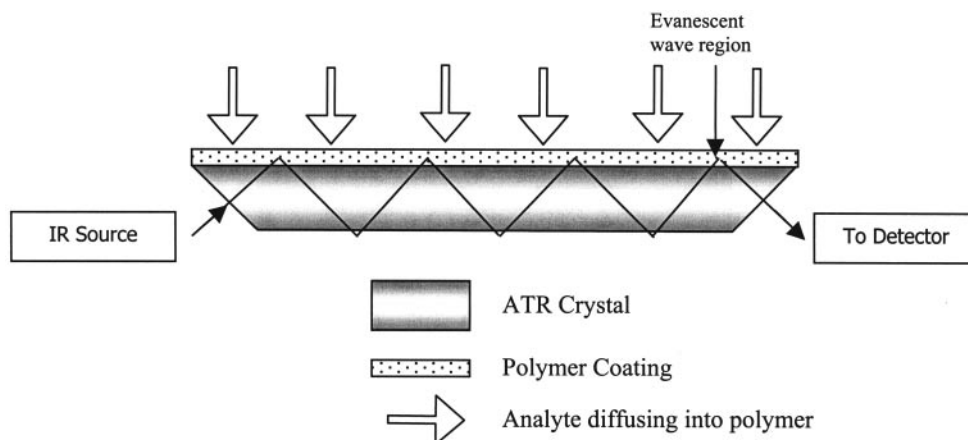


FIGURE 1 A trapezoidal design horizontal ATR crystal with a polymer cladding.

and flow-through techniques, and the diffusion coefficients were estimated using the stopped-flow model. Diffusion coefficient values of $2.4 \text{ E-}08 \text{ cm}^2 \text{ s}^{-1}$ (PIB) and $2.6 \text{ E-}09 \text{ cm}^2 \text{ s}^{-1}$ (E-Pco) were obtained.

Hong and Barbari [9] have investigated the diffusion of a range of solvents into a $3 \mu\text{m}$ coating of polyisobutylene using capillary column inverse gas chromatography (CCIGC). At 40°C , a diffusion coefficient of $1.77 \text{ E-}09 \text{ cm}^2 \text{ s}^{-1}$ was achieved for chloroform.

Göbel *et al.* [4] investigated the detection of aqueous phase chlorohydrocarbons (CHCs) using a MIR fibre optic sensor in the temperature range $0\text{--}20^\circ\text{C}$. The question of whether the diffusion of one analyte is affected by another was investigated by studying the diffusion of CHCl_3 along with monochlorobenzene and tetrachloroethylene (TeCE) into a $14.1 \mu\text{m}$ PIB film. No mutual interference at concentrations less than 100 mg/L was observed as a divergence within the 15% standard deviation range was maintained. Limits of detection in the range $1\text{--}50 \text{ mg/L}$ were found for most of the analytes. In general, the higher the analyte solubility in water, the less sensitive the system is, due to the reduction in the partition coefficient of the CHC between water and the polymer. Recent work by Mizaikoff *et al.* [10] has focused on marine monitoring of CHCs, using a remotely controlled MIR field sensor.

In this investigation, three THMs and one tetrahalomethane were analysed in the gaseous phase. The advantages to carrying out this type of work in the gaseous phase, from the point of view of sensor design, are threefold.

- The gaseous phase allows for a study of diffusion in the absence of competitive solubility effects caused by water.
- Water ingress into the polymer film does not affect analyte diffusion.
- The lifetime of the polymer cladding is prolonged.

The objectives of this work were to illustrate the potential of this optical sensor for the detection of halomethanes in the gas phase and to study factors affecting analyte diffusion into films of PIB and E-Pco. To date no reported detection of halomethanes apart from chloroform in the aqueous phase [7] by this polymer-modified ATR-FTIR technique has been published.

EXPERIMENTAL

Reagents

Chloroform (CHCl_3 , 99%), bromoform (CHBr_3 , 96%), chlorodibromomethane (CHBr_2Cl , 98%), dibromodichloromethane (CBr_2Cl_2 , 95%) and tetrachloroethylene (TeCE, 99.9%) were purchased from Sigma Aldrich Ltd. Decalin (99.5%) and THF were purchased from BDH. Sigma Aldrich Ltd. supplied polyisobutylene (PIB, M_w 4 700 000) and ethylene-propylene copolymer (60% E) (E-Pco, M_w 1 70 000). Zero-grade air was obtained from BOC Gases.

Materials and Equipment

A Bio-Rad FTS-7 Fourier-Transform Infrared spectrometer with a DTGS detector was used throughout these experiments. An ATR optical attachment and ZnSe IRE (dimensions: $7.2 \times 1.0 \times 0.6$ cm, 45° angle of incidence, 6 internal reflections) were obtained from Bio-Rad and incorporated into a steel housing. The flow cell had an internal volume of $500 \mu\text{L}$. TygonTM tubing, TeflonTM connectors and a three-way valve were used for the sampling lines. SKC TedlarTM sampling bags (40 and 80 L) were used in the preparation of the standards. A SKC rotameter was calibrated using a Humonics 650 digital calibrator to maintain a steady flow. A Gilian constant flow air-sampling pump was used to pump the gas through the system. Figure 2 illustrates the experimental system used.

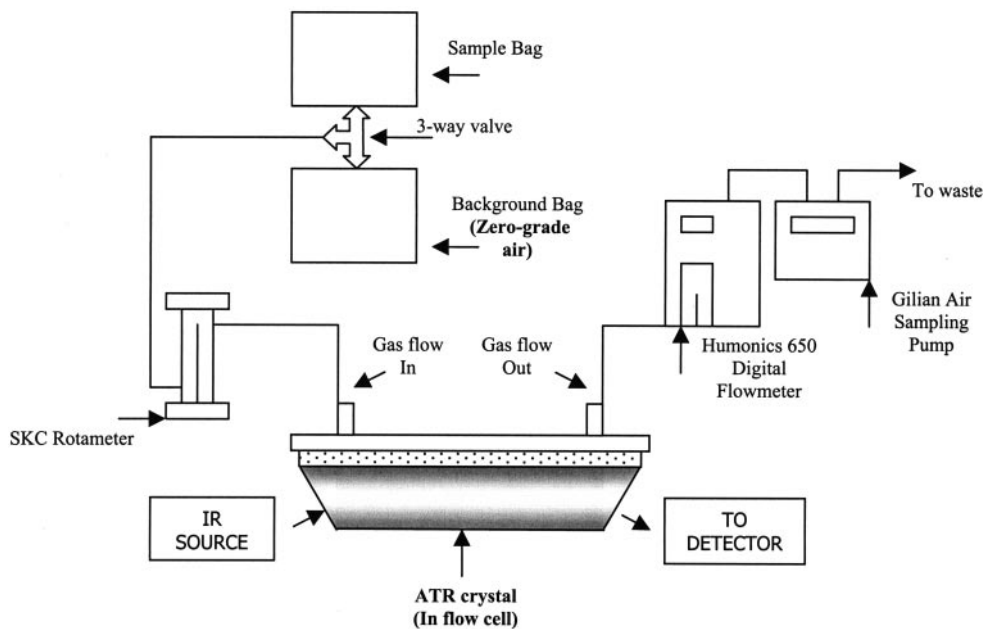


FIGURE 2 Instrumental design.

Polymer Coating Procedure

The ZnSe IRE was coated on the upper surface with a 2% (w/w) solution of the polymer under analysis. The polymers were dissolved in decalin and stirred until dissolution was complete. The solutions were then drop-coated onto the ATR crystal and allowed to dry in a desiccator. This facilitated slow evaporation of the solvent and was found to produce a smooth, even layer which was verified using SEM analysis. Finally, a flow of nitrogen was used to remove any residual solvent. The average thickness across the polymer film was taken and therefore average localised variations in the thickness were accounted for. The crystal was weighed before and after each coating and the thickness l of the layer was calculated according to Eq. (1),

$$l = \frac{m_e - m_0}{\rho \cdot A} \quad (1)$$

where l is the thickness of the layer (cm); m_0 is the weight of IRE before coating (g); m_e is the weight of the IRE after coating (g); ρ is the density of the polymer (g cm^{-3}) and A is the surface area of the IRE (cm^2).

The polymer layers were removed by washing with THF.

Preparation of Standards

The various gas standards were made up in TedlarTM sampling bags (40/80 L depending on analysis run times) using zero-grade air and allowed to equilibrate for 1 h.

For liquids the volume to be injected was calculated using Eq. (2) [3]:

$$V_1 = \frac{cMV_2}{D(24.54 \times 10^3)} \quad (2)$$

where V_1 is the liquid sample volume (μL); c is the concentration of the solvent (mg L^{-1}); M is the molecular weight; V_2 is the volume of air to be released into the bag (L); D is the liquid density in (g cm^{-3}) and 24.54×10^3 is the number of μL of vapour per millimole of analyte at atmospheric pressure and 22°C .

Experimental Procedure

Accurate flow rates were achieved by calibrating all flowmeters, using the digital calibrator. The flow rate for the system was previously optimised using tetrachloroethylene, over the range $0.2\text{--}1.5 \text{ L min}^{-1}$. A flow rate of 1.0 L min^{-1} was found to give optimum sensitivity. Standards were withdrawn from the sample bags by means of a Gilian sampling pump, through the rotameter and across the polymer membrane in the cell at the set flow rate. Zero-grade air was used as the background. A quantitation method was established using a Win-IR software package. The FTIR instrumental parameters used in all experiments are shown in Table I.

A selective band in the fingerprint region for each compound was used to detect the individual analytes. A corrected baseline was applied and absorbance values were based on peak areas. The main IR bands for the analytes of interest are shown in Table II

TABLE I FTIR (Bio-Rad FTS-7) instrumental parameters

<i>Parameter</i>	<i>Value</i>
Resolution	4 cm ⁻¹
Scan velocity	5 kHz
UDR ^a	2
Aperture	None
Sensitivity ^b	1
Filtre	1.12 kHz
Co-added scans per scan set	16
Number of scan sets	Varied (1–240)

^aUndersampling ratio – controls the rate of data collection;

^bSensitivity – adjusts the amplifier gain.

TABLE II Analyte IR absorption bands plus selected analyte properties [10,11]

<i>Analyte</i>	<i>Principle IR absorption band (cm⁻¹)</i>	<i>Band</i>	<i>Vapour pressure (kPa)</i>	<i>Molar volume (cm³ mol⁻¹)</i>
Chloroform	762	C–Cl Stretching	21.332@20°C	80.12@20°C
Bromoform	1142	C–H Bending	0.667@20°C	87.16@20°C
Chlorodibromomethane	748	C–Cl Stretching	6.093@17°C	87.52@20°C
Dibromodichloromethane	735	C–Cl Stretching	N/A*	99.77@20°C

*N/A denotes not available in the literature.

along with analyte properties, which are important for diffusion discussion purposes. It should be noted that the bands of the analytes used in the multicomponent analyses (CHCl₃ and CBr₂Cl₂) did not overlap, thus enabling them to be identified without the need for data manipulation techniques.

RESULTS AND DISCUSSION

All experiments were carried out at room temperature (22 ± 1°C). Diffusion coefficient values were calculated for each of the halomethanes diffusing into PIB and E–Pco. Diffusion coefficients were measured using a Fickian type mathematical model presented by Hong *et al.* [12] and incorporating analyte peak area. This vapour phase binary model incorporates similar boundary conditions to those of this work and was therefore considered applicable. The model used assumes a constant flow experimental design with the concentration of analyte therefore at the surface of the polymer being constant. The initial concentration at the surface of the polymer and thus at the crystal face is zero in all cases. The model also incorporates parameters such as refractive indices of the polymer and ATR crystal, polymer film thickness and the wavelength of the quantified peak. The depth of penetration value is calculated within the model.

The analyte wavenumber range extended from 1142 cm⁻¹ (CHBr₃) to 735 cm⁻¹ (CBr₂Cl₂). The refractive index (RI) value of the ZnSe crystal at these two extremes ranged from 2.412 (1142 cm⁻¹) to 2.385 (735 cm⁻¹). These RI values were entered into the model and the change in the diffusion coefficient was noted. The diffusion of CHBr₃ into PIB has an average diffusion coefficient of 3.38 E-10 cm² s⁻¹ and has

a standard deviation of $0.01 \text{ E-}10 \text{ cm}^2 \text{ s}^{-1}$ over the wavenumber range presented above. For CBr_2Cl_2 diffusion into PIB, an average diffusion coefficient of $3.70 \text{ E-}10 \text{ cm}^2 \text{ s}^{-1}$ has a standard deviation of $0.03 \text{ E-}11 \text{ cm}^2 \text{ s}^{-1}$ over the same wavenumber range. For subsequent analyses an average RI value was taken.

A line of best fit was determined for each experiment and the diffusion coefficient value estimated. Peak areas were determined by selecting a point at either side of the appropriate peak and applying a baseline.

The compounds were analysed individually and then as part of a mixture in the case of CHBr_3 and CBr_2Cl_2 , to ascertain whether or not multicomponent effects could be observed.

Ethylene-propylene copolymer and PIB were used because of their low glass transition temperatures and amorphous structures. In general, the lower the glass transition temperature, the higher the available free volume between polymer chains, which facilitates the diffusion of molecules through the membrane [7].

A typical 3D diffusion profile is shown in Fig. 3, which shows the diffusion of 1000 mg/L CBr_2Cl_2 into a $12.5 \mu\text{m}$ film of E-Pco. The quantified absorption peak is indicated at 735 cm^{-1} and is based on peak area. From this profile, the speed of diffusion of the halomethanes into the copolymer in general is demonstrated. In this case, the t_{90} saturation value is approximately 10 min. The t_{90} value, which is the time taken for the analyte absorbance to reach 90% of its equilibrium value, is comparable to liquid chromatographic run times. Also evident in this profile is the regeneration ability of this polymer-based sensor. An important feature of any sensor is regeneration time before subsequent analyses can be carried out. To estimate this time, zero-grade air was flushed through the system immediately after the sample by means of a three-way valve. Average regeneration times for the analytes into PIB ranged from 35 min for CHBr_3 to 18 min for CHCl_3 , the fastest of the analytes to diffuse in. Diffusion of the analytes out of E-Pco averaged 16 min for CHBr_3 to 3 min for CHCl_3 .

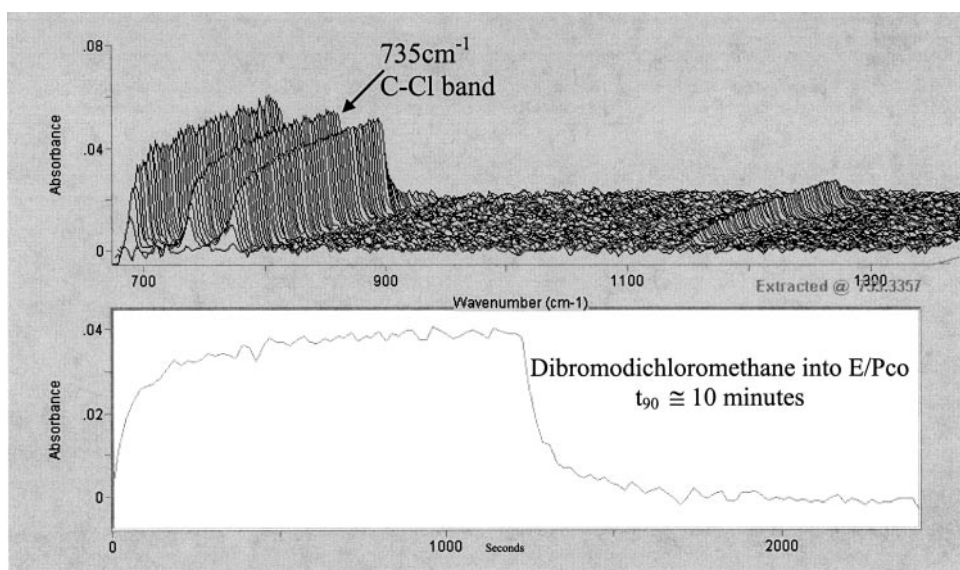


FIGURE 3 3D profile of the diffusion of 1000 mg/L dibromodichloromethane into a $12.5 \mu\text{m}$ E-P copolymer film at 22°C .

For each analysis theoretical results predicted using the Fickian diffusion model were compared with experimental diffusion profile results and the line of best fit was determined. Figure 4 demonstrates the diffusion of 1000 mg/L CHBr_3 into an $8.2\ \mu\text{m}$ film of E-Pco. Bharadwaj and Boyd [13] estimated the fractional free volumes of polyethylene (PE), polypropylene (PP) and PIB. The free volume between the polymer chains in PIB was found to be lower than that in PE and PP, which have the same free volume, and hence we are assuming a similar free volume for the copolymer. Diffusion into the copolymer is faster than into PIB with equilibrium absorbance values reached quicker. PIB has a large cross-sectional area that leads to more efficient packing of its molecules and thus a lower available free volume through which the solvent molecules can diffuse [13].

For both polymers, CHCl_3 (which is the smallest molecule analysed and has the highest vapour pressure) is the fastest diffusing compound, with diffusion coefficients of $4.72\ \text{E-}08 \pm 0.42\ \text{E-}08\ \text{cm}^2\ \text{s}^{-1}$ in E-Pco and $0.50\ \text{E-}08 \pm 0.01\ \text{E-}08\ \text{cm}^2\ \text{s}^{-1}$ in PIB (see Table III). The same order of diffusion of the analytes is observed for both polymers with CHCl_3 being followed by CHBr_2Cl , CBr_2Cl_2 and CHBr_3 , respectively.

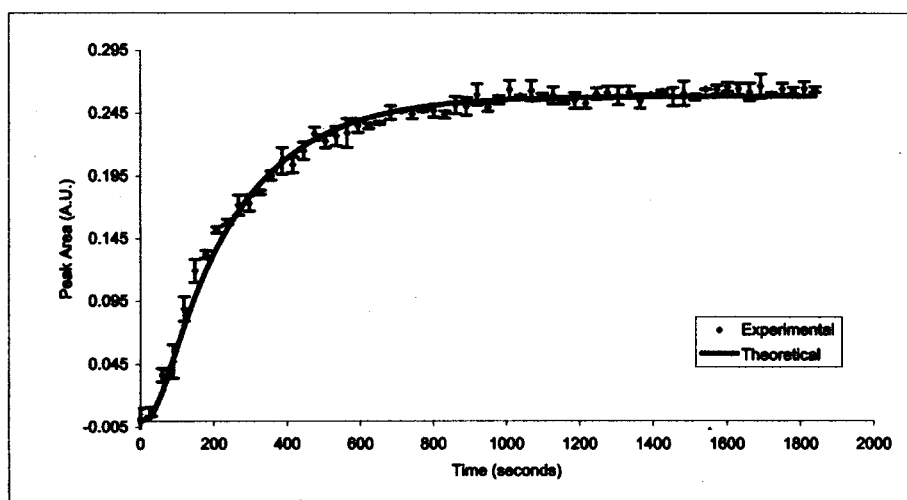


FIGURE 4 1000 mg/L bromoform diffusing into an $8.2\ \mu\text{m}$ E-P copolymer film at 22°C . Error bars are based on \pm one standard deviation obtained from replicate experimental runs.

TABLE III Single component diffusion coefficients for halomethanes (1000 mg/L) diffusing into a $12.5\ \mu\text{m}$ E-P copolymer film and $12/16\ \mu\text{m}$ PIB films at 22°C . Each diffusion coefficient is based on an average value obtained from 3/4 replicate runs, with error bars based on \pm one standard deviation

Analyte	Diffusion coefficient ($\text{cm}^2\ \text{s}^{-1}$)	
	E-P copolymer	PIB
Chloroform	$4.72\ \text{E-}08 \pm 0.42\ \text{E-}08$	$50.00\ \text{E-}10 \pm 1.41\ \text{E-}10$
Bromoform	$0.29\ \text{E-}08 \pm 0.03\ \text{E-}09$	$3.38\ \text{E-}10 \pm 0.01\ \text{E-}10$
Chlorodibromomethane	$1.31\ \text{E-}08 \pm 0.21\ \text{E-}08$	$29.30\ \text{E-}10 \pm 0.21\ \text{E-}10$
Dibromodichloromethane	$1.10\ \text{E-}08 \pm 0.14\ \text{E-}08$	$3.70\ \text{E-}10 \pm 0.17\ \text{E-}10$

It is also worth noting the relationship between the rates of diffusion of the analytes and the available literature values of vapour pressure and molar volume. The greater the vapour pressure the faster the diffusion. According to Berens and Hopfenberg [14] diffusivities of gases and vapours in PVC are strongly dependent upon the penetrant molecule size, as measured by the van der Waals' molar volumes. However, no correlation between analyte molar volumes and diffusion rates were evident in this study (see Tables II and III). The greater spread of diffusion coefficients evident for PIB in Table III, as compared to the copolymer, would point to its greater molecular sieving capability due to its lower free volume.

The applicability of this sensing system was investigated for multicomponent analysis. The principle absorption bands of CHBr_3 and CBr_2Cl_2 ($1142, 735 \text{ cm}^{-1}$) did not overlap, thus enabling them to be quantified without the use of data manipulation techniques. This illustrates a core advantage of this MIR optical sensor approach, namely, specificity and the ability to carry out multicomponent analyses.

As can be seen from Table IV, in the single-component analyses, CBr_2Cl_2 diffused into both PIB and the copolymer faster than CHBr_3 . In the copolymer CBr_2Cl_2 has a diffusion coefficient value of $1.10 \text{ E-}08 \pm 0.14 \text{ E-}08 \text{ cm}^2 \text{ s}^{-1}$ and CHBr_3 has a diffusion coefficient value of $0.29 \text{ E-}08 \pm 0.03 \text{ E-}09 \text{ cm}^2 \text{ s}^{-1}$. In the multicomponent analyses, the diffusion coefficient of CBr_2Cl_2 , the faster diffusing compound, remains virtually the same as the single component value, within one standard deviation. However, the diffusion coefficient value for CHBr_3 has increased to $0.33 \text{ E-}08 \pm 0.07 \text{ E-}10 \text{ cm}^2 \text{ s}^{-1}$ (Table IV). According to Hong *et al.* [12] the diffusion of the slower penetrant is affected by the concentration gradient of both penetrants while that of the faster penetrant may only be affected by its own concentration gradient. The slower penetrant appears to be influenced by the additional free volume introduced by the faster penetrant [12]. This supports the result data from our experiments. Again, in the case of PIB, the same trend is followed (Table IV). The diffusion coefficient of CBr_2Cl_2 has changed by less than one standard deviation, while that of CHBr_3 has increased, from $3.38 \text{ E-}10 \pm 0.10 \text{ E-}11 \text{ cm}^2 \text{ s}^{-1}$ to $4.33 \text{ E-}10 \pm 0.10 \text{ E-}10 \text{ cm}^2 \text{ s}^{-1}$.

From the above results, it is obvious that there is a need to carry out multicomponent diffusion experiments to quantify cross-diffusion effects as a means to optimise polymer-modified ATR-FTIR sensors.

Further investigation is required of the diffusion process as the polymer bands in the diffusion experiments have been studied and have not increased or decreased in absorption value over the course of our experiments. There would be an expected decrease in polymer band intensity if polymer swelling was the reason for the observed multicomponent effects in this work.

TABLE IV 1000 mg/L bromoform–dibromodichloromethane (single and multicomponent) diffusing into a $12.5 \mu\text{m}$ E–P copolymer film and a $12 \mu\text{m}$ PIB films at 22°C . Each diffusion coefficient is based on an average value obtained from 3 replicate runs, with error bars based on \pm one standard deviation

Polymer	Analyte	Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)	
		Single component	Multicomponent
E–P copolymer	Dibromodichloromethane	$1.10 \text{ E-}08 \pm 0.14 \text{ E-}08$	$1.14 \text{ E-}08 \pm 0.06 \text{ E-}08$
E–P copolymer	Bromoform	$0.29 \text{ E-}08 \pm 0.03 \text{ E-}09$	$0.33 \text{ E-}08 \pm 0.07 \text{ E-}10$
PIB	Dibromodichloromethane	$3.70 \text{ E-}10 \pm 0.17 \text{ E-}10$	$3.85 \text{ E-}10 \pm 0.06 \text{ E-}10$
PIB	Bromoform	$3.38 \text{ E-}10 \pm 0.01 \text{ E-}10$	$4.33 \text{ E-}10 \pm 0.10 \text{ E-}10$

CONCLUSION

The applicability of this sensing approach for the detection of halomethanes has been demonstrated. It is possible to use polymer modified ATR-FTIR for the rapid detection of halomethanes in the gas phase. Quantification of enrichment rates was achieved using a mathematical diffusion model. From the results, it can be seen that:

- A Fickian diffusion model provides a good fit to experimental diffusion profiles.
- Faster rates of diffusion of THMs are observed for diffusion into E-Pco than into PIB.
- The rates of diffusion from the gas phase through polymer films parallel literature values for analyte vapour pressure.
- Significantly, faster diffusing compounds affect the rate of slower diffusing compounds into E-Pco and PIB films.

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