O'Callaghan, Kristina and Fredericks, Peter M and Bromwich, David (2001) Evaluation Of Chemical Protective Clothing by FT-IR/ATR Spectroscopy. *Applied Spectroscopy* 55(5):555-562.

Evaluation Of Chemical Protective Clothing by FT-IR/ATR Spectroscopy

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An attenuated total reflectance permeation cell has been used to evaluate the permeation of polymer samples from chemical protective clothing (CPC), mainly gloves, by several chemical types including a solvent, a commercial pesticide mix, and a volatile solid. Good contact between sample and ATR crystal was ensured by the use of low gas pressure. The passage of the chemicals through the CPC sample could be readily followed by analysis of sets of FT-IR spectra measured during permeation experiments. Diffusion coefficients could only be estimated. The ATR method is compared with the traditional two-compartment cell used for evaluation of CPC, and its advantages and disadvantages discussed.

Index headings: **FT-IR; attenuated total reflectance; chemical protective clothing; polymer membrane; diffusion**

INTRODUCTION

Chemical protective clothing (CPC) is used to isolate parts of the body from direct contact with a potentially hazardous chemical. For example, the use of gloves when handling chemicals has become widespread. Such gloves may be made from a variety of polymers, polymer blends or polymer laminates, depending on the particular application. Glove materials which may be highly effective for one chemical may be totally ineffective for another. For this reason it is important to test the permeability of the wide range of available materials by the particular chemical to be handled.

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A substance might pass through a CPC membrane by two possible processes: penetration or permeation[1]. Penetration is a macro scale breach of the CPC through discontinuities in the material, such as a pinhole. Permeation is a process whereby a substance moves through a CPC material at a molecular level. Permeation is most frequently explained by a solution-diffusion model[2] which suggests three steps for the process: dissolution of permeant in the membrane, diffusion of permeant through the membrane, and evaporation/desorption from the other side of the membrane. The work described in this paper is concerned only with permeation.

The conventional method for testing CPC for permeation by chemicals is by the use of a two compartment cell as described in the ASTM F739-99 Standard. In this type of cell the test chamber consists of two compartments separated by the test material. One side of the material is exposed to the test chemical in either a stopped or continuous flow set-up. Any species which permeates the test material is collected by a flowing carrier stream of liquid or gas in the second compartment. The permeant concentration is then measured by some conventional analytical technique to yield a permeation rate vs time plot. Nelson *et al.*[3] identified five types of permeation behaviour depending on the degree of interaction of the chemical with the test material, ranging from no interaction, through swelling of the polymer material, to catastrophic failure caused by dissolution of the test membrane. The parameters which may be measured for a CPC sample in a two-compartment cell are the breakthrough time (BT) and the steady state permeation rate (SSPR). This information can be used, together with toxicity information, to rank the suitability of CPC materials to the particular challenge chemical. The important variables of the two-compartment cell, which can affect the measurement of BT and SSPR, are the volume of the collecting chamber, the nature of the flow system (open or closed loop), the collection medium (which must not affect the CPC membrane), the exposed area of sample, the temperature, and the sensitivity of the analytical system[4].

Where the permeating chemical is either insoluble in the collecting fluid, usually water, or does not evaporate into a collecting gas stream, other collecting media such as silicone rubber have been tried, with limited success.[5] An alternative approach to the measurement of permeation of small molecules through CPC materials is by infrared spectroscopy utilising the attenuated total reflectance (ATR) sampling technique. When combined with a Fourier transform infrared (FT-IR) spectrometer the ATR technique can be rapid and sensitive, consequently there have been a number of reports of the use of FT-IR/ATR to study chemical transport through polymer systems[6-30]. A review of this technique has been published by van Alsten[10]. Much of the work deals with the measurement of diffusivities of small molecules through cast polymer films, which naturally make good contact with the ATR crystal. Only recently has it been recognised that the ATR approach may be applicable to manufactured polymer films, where contact with the ATR crystal is a parameter that must be addressed[11,13]. The ATR technique has not yet been widely applied to the evaluation of CPC materials, and only one report has been found in the literature[12].

As mentioned above, one of the problems associated with ATR of manufactured polymer membranes, such as those used for CPC, is to maintain good and reproducible contact with the ATR crystal. Semwal et al.[11] studied the transport of sulfur mustard and oxygen mustard in polypropylene by exposing one surface of a film sample to the chemical, sealing this surface with tin foil and then measuring the appearance of the chemical at the other surface by ATR/FT-IR spectroscopy. Good contact between the film and the ATR could be maintained by a mechanical clamp arrangement, because exposure to the chemical and ATR measurement were separate parts of the experiment. Accurate measurement of breakthrough time was not possible using this method. A more interesting approach has been taken by Bromwich,[12] and subsequently by Balik and Simendinger,[13] who developed ATR cells in which good contact between the film and the ATR crystal was maintained by gas pressurisation with an infrared inactive gas at pressures in the range 1 - 3.3 atm. This approach allows continuous exposure of one surface of a membrane to a chemical, at the same time as the ATR spectroscopy is being measured on the other surface.

This paper describes the use of a gas pressurised ATR cell to evaluate the performance of CPC materials exposed to chemicals and shows that this approach has the potential to be simpler and quicker than conventional methods. The method is applied to a range of materials exposed to a solvent, a solvent-water mixture, a volatile solid, and a commercial pesticide formulation.

EXPERIMENTAL

ATR Diffusion Cell. The gas pressurised diffusion cell was a modification of a commercially available horizontal ATR accessory (Graseby-Specac, Crayford, Kent, UK) equipped with a ZnSe crystal of dimensions 1 cm x 5 cm, and an angle of incidence of 45°. A schematic of the cell is shown in Fig. 1. The upper cell body has internal water channels machined into it and may be temperature controlled by means of flowing water. The cell base may be heated electrically. The cell body is designed to fit over the crystal in its holder and to seal the sample to the crystal holder around the perimeter of the crystal. The cell body has a hollow section which formed the permeant chamber when the cell was assembled. Sealing between the crystal holder, the CPC sample and the cell body was achieved by a 50 μm high raised rectangular lip on the underside of the cell body, which encircled the crystal when the cell was assembled. The aluminium cell base was simply screwed onto the mirror assembly in place of the normal top plate of the ATR accessory.

A background spectrum was obtained through the empty ATR accessory. A spectrum of the CPC material under test was acquired prior to addition of the permeant. Pressure was removed briefly whilst permeant was added to the cell. For liquids, permeant addition was achieved through the gas line opening in the lid of the cell. For solids addition the lid was removed briefly. A lead weight, machined to fit the void in the permeant chamber, was used to ensure packing of solids against the CPC material.

One benefit of the cell was that it was sealed, so that toxic test chemicals could be added, and the cell disassembled and cleaned in a fume hood, with no possibility of leakage of liquids or vapours while ATR measurements were being carried out. In use the cell was pressurised at 0.6 atm by dry nitrogen which ensured good contact between the sample and the crystal. Most measurements described in this paper were made at ambient temperature (about 20^{o}C), but a few measurements were made at temperatures of 38^{o}C and 45^{o}C by activating the heating elements in the cell base. Temperature control for elevated temperature experiments was achieved using a thermocouple and a Specac temperature controller.

Spectroscopy: The ATR accessory with diffusion cell was mounted in a Perkin Elmer Series 2000 FT-IR spectrometer equipped with a KBr beamsplitter and a DTGS detector. Spectra were acquired at 8 cm^{-1} resolution in the spectral range 4000 – 700 cm^{-1} using an OPD velocity of 2 cm s^{-1} and strong Beer-Norton apodization. Data were acquired using Spectrum for Windows software (Perkin Elmer Corp., Norwalk, CT, USA). Four scans were co-added for each of the time-resolved spectra collected during a permeation experiment, leading to a typical rate of data collection of one spectrum every 30 s. Spectral manipulation was performed using GRAMS software (Galactic Industries Corp., Salem, NH, USA). Breakthrough time (BT) was taken to be the time immediately preceding the time at which two or more consecutive absorbances exceed three standard deviations from the background absorbance. The results of replicate experiments are reported as the mean BT $\pm$ 2 standard deviations.

Materials: The reference neoprene sample, of nominal thickness 0.41 mm, was obtained from ASTM Committee F-23, and is that used in the interlaboratory trial of the standard method ASTM F 7391. Samples (approximately 90 mm x 30 mm) used to test the permeation cell were cut from commercially available gloves. Two thicknesses of latex gloves were used, standard gloves around 0.43 mm, and examination gloves with a thickness around 0.11 mm. Nitrile rubber gloves of two thicknesses, approximately 0.28 and 0.32, were also used. Sample thickness was determined using a micrometer screw gauge, to an accuracy of $\pm$ 5 μm.

Acetone (analytical reagent grade) and toluene (general purpose reagent grade) were obtained from BDH Chemicals and were used as received. Naphthalene flakes (Ormond Apex Products) were commercially available, as was a concentrated malathion-based pesticide formulation (Authur Yates & Co. Ltd, Sydney, Australia).

RESULTS AND DISCUSSION

Effect of Gas Pressure. It is important to investigate whether the gas pressure used to maintain contact between the membrane and the internal reflection element (IRE) has any effect upon the measured permeation properties. If permeation follows the solution-diffusion model, then there should be no effect from the small pressures used in this experiment. However, if any membrane with a connected pore structure is tested, then pressure might be expected to affect the permeation rate and BT.[31]

Pressures of 0.6 and 1.3 atm were tested. The maximum pressure was limited because of the possibility of damage to the IRE which could become dislodged from its metal holder by excessive pressure. Initially, the effect of pressure was tested with only the membrane present. As expected increased pressure improved the contact slightly and increased the intensity of polymer absorption bands. However, it was noticed that there was a high level of baseline drift within and between different experiments. This was traced to the trapping of an air bubble between the membrane and the IRE. The experimental procedure was modified so that final tightening of screws to seal the membrane to the IRE surface was performed after the cell was pressurised to the desired level. This minimised air trapped between the IRE and the membrane and following the modification repeated spectra taken over periods up to 30 min with only the membrane present were very consistent.

When acetone was present as the permeant, the results of experiments at 0.6 and 1.3 atm did not show any significant differences beyond the normal experimental variation. Consequently, the lower pressure, 0.6 atm, was used for further experiments to minimise risk of damage to the IRE.

The performance of the ATR cell for the measurement of permeation of small molecules through CPC materials was assessed by the use of several permeants: acetone, acetone/water mixtures, naphthalene, and a commercial pesticide formulation based on the active component malathion. The materials tested for permeation were latex, neoprene or nitrile rubber.

Acetone/Neoprene. The study of the permeation of standard neoprene by acetone allowed the reproducibility of the ATR method to be investigated. Fig. 2 shows some of a typical set of spectra obtained from this permeation experiment carried out at ambient temperature. The early spectra show bands due only to the neoprene, but after about 2000 s the acetone has permeated the neoprene and is apparent in the spectra, particularly the carbonyl stretching band near 1720 cm^{-1}. There is also an increase in the band near 2220 cm^{-1}, due to atmospheric CO_2 as the acetone bands increase. We do not currently have an explanation of this phenomenon.

Measurement of the area of the carbonyl stretching band of the acetone versus time for four repeats of this permeation experiment showed that while the breakthrough time of around 1000 s was reasonably consistent, the rate of diffusion of the acetone appeared not to be very reproducible for the four experiments. However, if the acetone absorbance is ratioed to the absorbance of a neoprene band, then the reproducibility is significantly improved (Fig. 3). This normalisation technique has been applied previously to spectra from FT-IR/ATR permeation experiments with polymers where the sample was not cast from solution directly onto the ATR crystal[11-13,25]. The rationale behind the band ratioing procedure is that if contact between the sample and the ATR crystal improves, a larger volume of polymer will be measured by the evanescent wave. The absorbance of permeant dissolved in the polymer will also increase in proportion. Hence the polymer can act as an internal standard. Variation in contact is to be expected as the permeant moves through the polymer because of swelling, change in stiffness etc. Once permeant begins to “pool” in the voids between the polymer and the ATR crystal, the band ratioing method will become less effective because the pooled permeant is not closely linked with the polymer. However, it is evident that for the case of acetone permeating neoprene, contact is a major variable and can be overcome by the band ratio method.

BTs for the four experiments shown in Fig. 3 gave a mean BT of 16.7 ± 1.9 min. This result is in reasonable agreement with previous results reported by Berardinelli et al.[32] (14-15 min) and Mellstrom et al.[33] (14-17 min), using a two compartment cell, for acetone permeation of similar, but not identical, neoprene membranes. BT is affected by the sensitivity of the analytical method, as well as the frequency of analytical measurements during a permeation experiment.

Acetone-Water Mixture/Nitrile Rubber. The capability of the FT-IR/ATR method to measure mixtures was examined by the use of a 40% w/w acetone-water mixture permeating nitrile rubber from a commercially available glove. Both water and acetone permeate nitrile rubber within the timeframe of this experiment. Water alone permeates nitrile rubber rather slowly, but its dissolution and permeation in the nitrile rubber are much enhanced by the presence of the acetone. Fig. 4 shows a set of spectra obtained for this permeation experiment. The appearance of both the O-H stretching band of the water near 3500 cm^{-1}, and the C=O stretching band of the acetone near 1720 cm^{-1}, are clearly visible in the spectra.

Figs. 5 and 6 show plots of the area ratio of the carbonyl band and the hydroxyl band, respectively, using the 2240 cm^{-1} band of the nitrile rubber for ratioing purposes. The plots show the results of six replicate experiments. Both plots seem to show less reproducibility than that obtained for acetone/neoprene, and the measurement of the hydroxyl band of water appears significantly less reproducible than that of the carbonyl band of the acetone. The lower reproducibility of the hydroxyl band measurement is probably due to the broadness of the hydroxyl stretching absorbance band, compared with that of the carbonyl band. This would certainly have an impact on BT because of the difficulty of determining the presence in a spectrum of a weak broad band. Another source of variability may be the polymer membrane itself which may have considerable thickness variation within, and between, samples cut from manufactured CPC such as gloves. The high level of variability of nitrile gloves between batch lots from the same manufacturer has been documented.[34]

The mean BTs for the acetone and the water permeation in six replicate experiments for the permeation of acetone-water mixtures through nitrile rubber were 56 ± 7 min and 29 ± 4 min, respectively. It is interesting to note that when nitrile rubber is permeated by acetone or water, separately, the acetone permeates much more quickly than the water. However, in the acetone-water mixture experiment, the ATR spectra clearly show that the water permeates considerably more quickly than the acetone. It may be that a small proportion of the acetone (below the ATR detection limit) rapidly permeates the nitrile rubber material which changes the nature of the material to allow rapid permeation by water, followed by slower permeation by the bulk of the acetone.

Naphthalene/Latex Rubber. Solids possessing a substantial vapour pressure at ambient temperature are capable of permeating CPC materials. The standard two-compartment cell is designed for use with liquid or gaseous test chemicals and although it has been modified for use with solids[35,36], it is still somewhat limited in its application. The ATR cell is quite suitable for the study of solids and requires only that the sample solid be placed in the permeant chamber. A machined lead weight was placed on the sample to force it against the CPC material to simulate a workplace situation where solid is being handled.

Fig. 7 shows a series of spectra, in the region 950 – 700 cm^{-1}, showing the permeation of naphthalene, as commercially-available flakes, through latex rubber, a common material for general purpose gloves. The aromatic C-H bending mode at 780 cm^{-1} is a clear indicator of the permeation of naphthalene. For gloves of nominal thickness 0.134 mm the breakthrough time for naphthalene was in the range 2.7 – 3 min. This is consistent with the 4.3 $\pm$ 0.2 min obtained by Fricker and Hardy[35,36] for different latex glove material of nominal thickness 0.127 mm, using a modified two-compartment cell. It appears that the FT-IR/ATR detection system has comparable sensitivity to naphthalene as the gas chromatograph with flame ionisation detector used by Fricker and Hardy.

Effect of Temperature. An increase in temperature will increase the permeation rate and decrease the breakthrough time. While most CPC is used at around ambient temperature, certain protective articles, such as gloves, may attain a temperature close to that of the human body. The standard two compartment cell method[1] allows for temperature variation by having the cell immersed in a constant temperature bath or chamber. With the ATR cell temperature variation is easier because of electrical heating of the metal block that incorporates the IRE. Examples of the influence of temperature variation on permeation are shown in Figs. 8 and 9. Fig. 8 shows the effect of temperature on the permeation of latex glove material by naphthalene. The BT decreases markedly from nearly 3000 s at 20°C, to around 1500 s at 38°C, and then further to around 800 s at 45°C. Fig. 9 shows how the permeation of a 40% acetone-water mixture through nitrile rubber varies with temperature in the range 20-45°C.

Calculation of Diffusion Coefficients. Assessment of the suitability of a material for CPC against a particular substance generally requires knowledge not only of the breakthrough time, but also of the permeation rate, which is the maximum flux through the material at steady-state. Permeation rate can be measured by the standard two compartment cell because the permeant is continuously being removed after passing through the membrane.[1,3] In contrast, the ATR experiment measures the concentration in a thin layer of the membrane adjacent to the IRE, and the rate at which this concentration changes over the course of a permeation experiment. Complications arise because the permeant pools between the IRE and the membrane, instead of being continually removed. For this reason the FT-IR/ATR experiment is not well suited to the measurement of permeation rate. However, the method can be used to determine a diffusion coefficient which is a measure of the resistance of the membrane to permeation by a particular substance.

Several different methods[18,28,29] have been used in the literature to calculate diffusion coefficients of species diffusing through polymers from FT-IR/ATR data. Most of these involve the assumption that the diffusing species follows Fickian diffusion, and are generally an approximation for long or short diffusion times. Each technique makes different assumptions, so the diffusion coefficients calculated from them are likely to be slightly different. The methods used to calculate the diffusion coefficient are outlined below. As discussed in the introduction, the approach used by most researchers in FT-IR/ATR studies of diffusion through polymers to date has been to fit the data to an expression based on the following relationship between absorbance and the diffusion coefficient, which is derived from the interaction of the exponentially decaying sampling beam with a Fickian diffusion profile[18]:

$$\frac{A}{A_\infty} = 1 - \frac{8\gamma}{\pi(1-e^{-2\gamma L})}\sum_{n=0}^{\infty}\frac{e^{g}\,(fe^{-2\gamma L} + (-1)^{n}(2\gamma))}{(2n+1)(4\gamma^{2} + f^{2})} \qquad \textbf{Equation 1}$$

where

$$f = \frac{(2n+1)\pi}{2L}, \qquad g = \frac{-D(2n+1)^{2}\pi^{2}t}{4L^{2}}$$

and

A	is the absorbance at time t
A_∞	is the absorbance at equilibrium
L	is half the thickness of the membrane
n	is the refractive index of the membrane material
D	is the diffusion coefficient
γ	is the reciprocal of the ATR penetration depth[37], i.e. the distance to which the evanescent wave decays to 1/e of its value at the interface

Equation 1 may be simplified by ignoring all but the first term of the summation[18]:

$$\frac{A}{A_\infty} = 1 - \frac{8\gamma}{\pi(1-e^{-2\gamma L})}\, x\, \frac{e^{\frac{-D\pi^{2}t}{4L}}\, x\left(\frac{\pi}{2L}e^{-2\gamma L} + 2\gamma\right)}{\left(4\gamma^{2} + \frac{\pi^{2}}{4L^{2}}\right)} \qquad \textbf{Equation 2}$$

To allow greater ease in fitting the data to Equation 2, it was further simplified by combining constants and rearranging slightly to:

$$A = a(b - e^{-ct})$$

Equation 3

where $a = \dfrac{8A_\infty\gamma\left(\frac{\pi}{2L}e^{-2\gamma L} + 2\gamma\right)}{\pi\left(1-e^{-2\gamma L}\right)\left(4\gamma^{2} + \frac{\pi^{2}}{4L^{2}}\right)}$

$$b = \frac{\pi\left(1-e^{-2\gamma L}\right)\left(4\gamma^{2} + \frac{\pi^{2}}{4L^{2}}\right)}{8\gamma\left(\frac{\pi}{2L}e^{-2\gamma L} + 2\gamma\right)} \qquad = \qquad A_\infty a^{-1} \quad (\text{ie } ab = A_\infty)$$

and $c = \dfrac{D\pi^{2}}{4L^{2}}$

Thus the data was fitted to three adjustable parameters. For data measured for the permeation of acetone through neoprene it was found that an expression of this form most closely fitted the data at longer times (>2000 s), than shorter times (about 1000 – 1500 s). The assumption has been made that the depth of sampling of the evanescent field remains constant. This may not be the case, as the presence of the diffusant in the polymer may change the refractive index of the sample, thus changing the sampling depth.

An alternative approach which allows the calculation of diffusion coefficients from short time permeation data is the lag time method which has been previously applied to FT-IR/ATR data.[11,30] The lag time is measured from the early portion of the permeation data by the method shown in Fig.10. Lag time (t′) is related to the diffusion coefficient by the simple expression: [38]

$$\text{Lag time } (t') = L^2/6D$$

The ATR equivalent of the plot shown in Fig. 10 would be the absorbance versus time plot. The levelling off of the curve is because of membrane saturation, which does not occur in a two compartment cell system with a large collection volume or "open loop" flow of collection fluid. This means that the linear part of the curve, indicating a constant rate of permeation is limited, and so the lag time is measured using the region of maximum slope. A further difficulty is that the evanescent field decay is not taken into account by this technique, which could represent a considerable source of error. However, Semwal et al.[11] and Banerjee et al.[30] compared diffusion coefficients determined by this approach with those determined from standard mass sorption experiments for the permeation of oxygen mustard and sulfur mustard through various polymer membranes and found the results to be in very good agreement. This seems to indicate that the simplifications inherent in applying the lag time equation to FT-IR/ATR data do not have a significant impact on the accuracy of diffusion coefficient estimates. Indeed, Semwal et al.[11] and Banerjee et al.[30] achieved better agreement with the mass sorption data, than did Farinas et al.[25] who compared diffusion coefficients for urea permeating silicone films, determined from FT-IR/ATR data using a simplified version of Equation 1, with a radioactive tracer method for the same system. We therefore believe that the lag time method is appropriate for application to CPC because it is simple to apply, and because it uses short time data so that lengthy permeation experiments are not required.

Commercial Pesticide Preparation. To examine the use of the ATR method to test CPC performance for a more realistic workplace situation, the permeation of a commercial pesticide preparation, malathion, through nitrile rubber glove material was examined. The particular preparation was a concentrate of the active compound maldison (500 g L^{-1}) with toluene (435 g L^{-1}). Maldison, the O,O-dimethyl phosphorodithioate ester of diethyl mercaptosuccinate, is toxic, in common with other organophosphate compounds. The use of CPC when handling these materials is highly recommended. It was tested for permeation through two kinds of nitrile rubber glove material, one of nominal thickness 0.13 mm, while the other was of nominal thickness 0.32 mm. These gloves were from different manufacturers. IR spectra indicated that the thin gloves contained substantial amounts of carbonate filler, whereas the thicker gloves appeared to be unfilled.

Figure 11 shows the permeation behaviour of the toluene in the concentrate through the thick nitrile rubber material, compared with the permeation of pure toluene using the aromatic C-H bending vibration at 730 cm^{-1}, which was free of interferences from both nitrile rubber and maldison absorption bands, ratioed to the 2240 cm^{-1} band of the nitrile rubber. The BT for the toluene in the malathion concentrate (about 83 min) is much higher than for the neat toluene because the concentration is lower in the concentrate, and perhaps also because of other effects such as higher viscosity. For the thinner glove material, the BT for pure toluene was a matter of only a few seconds, while the BT for the toluene in the concentrate was about 3 min.

Maldison has absorption bands in its IR spectrum at 1735, 1012 and 820 cm^{-1} which might be used to follow permeation. The 1012 cm^{-1} band was found to be the most sensitive and readily measured and permeation data for maldison through thick nitrile rubber glove material is shown in Fig 12. The BT can be seen to be around 100 min. For the thin nitrile rubber glove material the BT was found to be rather low at about 4 min. Diffusion coefficients were estimated using the lag-time method and are shown in Table 1 for both types of glove material for neat toluene, and for toluene and maldison in the pesticide concentrate. Analysis of these data indicates that the thicker gloves are better to protect against both toluene and maldison in the concentrate, not only because they are thicker, but also because the material has a lower diffusion coefficient and is therefore more resistant to permeation by the maldison/toluene mixture.

The above results demonstrate that the properties of the two glove materials with respect to the two components of the commercial malathion concentrate, toluene and maldison, are easily and quickly measured at the same time, by the ATR method. The superior properties of one of the glove materials is immediately apparent.

CONCLUSIONS

Traditional CPC test techniques are limited to testing materials for protection against gases and volatile or water soluble liquids because they measure the flux of test chemical through the membrane using a two chambered permeation cell design. It is necessary to use a collector stream to carry any permeating material for further analysis. The FT-IR/ATR technique substitutes the collecting chamber with an IRE, so instead of measuring flux through the membrane, the amount of material reaching the innermost layer of the glove is measured directly. This eliminates the need for a collecting medium. It also allows easy testing of solids because the glove is supported by the IRE, eliminating the problem of achieving good contact between the glove and the solid without distorting the membrane.

To enable FT-IR/ATR to be used for CPC evaluation an ATR permeation cell, which uses gas pressure to achieve good optical contact between CPC membranes and the IRE, was designed and built. The pressure applied was not found to have a significant effect on permeation for the range 0.6 – 1.3 atm. Thus a pressure of 0.6 atm was used for CPC testing.

The applicability of the FT-IR/ATR cell for testing a variety of permeant/CPC systems was demonstrated by studying a simple liquid mixture (acetone/water), a solid (naphthalene), and a commercial pesticide formulation (malathion). The multi-wavelength detection of the FT-IR technique allowed permeation behaviour of individual components of mixtures to be monitored separately. The cell's electrical heating element allowed the effect of temperature on permeation to be studied.

The most important parameter for the assessment of CPC barrier effectiveness is the breakthrough time. The ease with which breakthrough times can be measured using the FT-IR/ATR permeation cell has been demonstrated. The second parameter, steady state permeation rate, cannot be measured using the FT-IR/ATR technique, however diffusion coefficients, estimated by the lag time method, were used as an alternative indicator of the protection offered by a given material against a given permeant. The FT-IR/ATR technique is therefore demonstrated to be a useful technique for assessing the barrier performance of CPC materials against a variety of chemicals.

ACKNOWLEDGMENT

The authors thank Dr. L. Rintoul for many helpful discussions.

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FIGURE CAPTIONS

1. Schematic diagram of gas pressurised ATR permeation cell
2. A typical set of ATR spectra obtained from the permeation of neoprene by acetone
3. Area of acetone carbonyl band for four replicate experiments of the permeation of neoprene by acetone, with correction for changing polymer contact by ratioing to the area of the 830 cm^{-1} neoprene absorption band.
4. A typical set of ATR spectra obtained from the permeation of a mixture of acetone (40% v/v) in water through nitrile rubber.
5. Ratio of area of the carbonyl band of acetone to that of the 2240 cm^{-1} band of the nitrile rubber for 5 replicate permeation experiments of a mixture of acetone (40% v/v) and water through nitrile rubber.
6. Ratio of the area of O-H stretching band of water to that of the 2240 cm^{-1} band of the nitrile rubber for 6 replicate permeation experiments of a mixture of acetone (40% v/v) and water through nitrile rubber.
7. A typical set of ATR spectra obtained from the permeation of naphthalene through latex.
8. Effect of temperature on the permeation of naphthalene through thick (0.32 mm) latex glove material by measurement of the 780 cm^{-1} band. Replicate experiments at 45^{o}C (x), 38^{o}C (Δ), and 20^{o}C (O).
9. Effect of temperature on the permeation of acetone through nitrile rubber from a 40% acetone-water mixture using the 1710 cm^{-1} carbonyl band of acetone ratioed to the 2240 cm^{-1} band of the nitrile rubber. Replicate experiments at 45^{o}C (أ), 38^{o}C (●), and 20^{o}C (x).
10. Example of the measurement of lag time by extrapolation of the linear region of the plot of cumulative permeation versus time.
11. Comparison of the permeation behaviour, for replicate experiments, of toluene in the malathion concentrate (أ) and pure toluene (x) through thick nitrile rubber glove material
12. The permeation behaviour, for two replicate experiments, of maldison in malathion concentrate through thick nitrile rubber glove material.

Table 1. Breakthrough times and diffusion coefficients for malathion concentrate and toluene through two types of nitrile rubber glove material.

Permeant	0.13 mm gloves		0.32 mm gloves	
	Breakthrough time (min)	Diffusion Coefficient ($m^2 s^{-1}$)	Breakthrough time (min)	Diffusion Coefficient ($m^2 s^{-1}$)
neat toluene	0.6	8×10^{-11}	28.3	9×10^{-12}
malathion concentrate				
toluene	2.9	1×10^{-11}	83.3	3×10^{-12}
maldison	4.3	7×10^{-12}	100.8	2×10^{-12}