The Design of Permeation Cells for Testing Chemical Protective Clothing

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ABSTRACT

Innovative permeation cells for measuring the permeation of chemicals through chemical protective clothing were developed, suitable for use with solids, liquids, gases and vapours under conditions of continuous and intermittent exposure. Mathematical modelling of permeation complemented these developments. Both approaches were used to increase the understanding of the effect of test conditions on permeation, the interpretation of the permeation data and the application of permeation indices.

An existing permeation cell, the Griffith cell, was validated against the standard American Society for Testing and Materials (ASTM) F739 permeation cell. An improved two-compartment permeation cell for continuous exposure, the “Griffith Mk2” cell, was developed to satisfy a comprehensive set of design criteria. This cell was also shown to be equivalent to the standard cell, but with improved collecting flow characteristics to efficiently remove permeant from the test sample. The cell could be used over a wide range of collecting flow rates without distorting the test sample. Operational parameters that could affect the measurement and interpretation of permeation data for conditions of continuous exposure, including collecting flow rate, collecting flow pattern, and solvent depth, were examined, but none were significant with the normal use of the Griffith Mk2 cell. Sample thickness measurement methods and techniques were also investigated. Trials with neoprene revealed a small chemical peak immediately on the addition of acetone that was attributed to initial stresses in the neoprene created by the acetone, releasing contaminants from the neoprene. Monitoring of the cells was performed with an eight channel automated permeation test system.

Modelling effects of detection limit on permeation indices showed Lag Time to be superior to Breakthrough Detection Time in discriminating choices of chemical protective clothing, and contrary to published views, was almost independent of the permeation detection limit. Experimental Lag Times were more precise than Breakthrough Detection Times and overcame the problem of carry-over between cells when testing with multiple cells and a single detector.

A novel gas pressurised permeation cell for CPC using attenuated total reflection and using Fourier Transform Infra-red spectroscopy was developed and demonstrated with naphthalene, a difficult-to-measure chemical which is water insoluble and known low
permeation rates. It circumvented the requirement for the chemical to evaporate or dissolve in a collecting medium and permitted the testing of samples without any sample preparation as the sample was in direct contact with attenuated total reflectance crystal. Detection of permeation occurred within the last two microns of the sample.

Intermittent exposure cell design criteria were developed and an automated intermittent permeation cell, based on the Griffith Mk2 cell, was developed for testing chemical protective clothing under conditions of intermittent exposure. Evaporation of acetone between exposures produced rapid cooling of the test sample and a corresponding drop in the permeation rate. Neoprene pre-exposed to acetone vapour produced the same permeation curves as that published in the ASTM standard for intermittent exposure.

A modified solution to the Crank-Nicolson Implicit numerical model of diffusion was used to describe permeation patterns for intermittent exposure. In interpreting intermittent exposure, several permeation indices were considered. Peak permeation rate was considered to be an important index for chemicals that have a threshold in their toxic action, such as skin irritants, but for irritants and other toxic chemicals, where a build-up of chemical is important, cumulative permeation is the appropriate index. When exposures were infrequent, the peak permeation rate was equivalent to that for independent exposures. For more frequent exposures, the cumulative permeation could be estimated by the total exposure time. Under realistic standardised conditions, random exposures produced maximum permeation rates twice that of regular cyclic exposures, but the cumulative exposure varied little. The solution required a diffusion coefficient that was exponentially concentration dependent to produce a good fit with experimental data.

**Keywords:** diffusion, permeation, chemical protective clothing, permeation cells, intermittent exposure, FTIR-ATR, models, occupational hygiene, solvents, polymer
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STATEMENT OF ORIGINALITY

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

David Bromwich
MATERIAL PUBLISHED IN THE COURSE OF THIS WORK


Notes:

The 1997 report by Bromwich, Smith and Yu was peer reviewed by external reviewers appointed by Worksafe Australia. It is available as a "PDF" file from the author's homepage, presently [http://wilbur.ens.gu.edu.au/hygiene/db.htm](http://wilbur.ens.gu.edu.au/hygiene/db.htm). PDF (Portable Document Format) files can be viewed and printed using the free Adobe Acrobat Reader 3.0 from [http://www.adobe.com](http://www.adobe.com).

AVAILABILITY OF DATA

The author will consider any approaches for experimental data from this work for comparative studies. His e-mail address is [D.Bromwich@mailbox.gu.edu.au](mailto:D.Bromwich@mailbox.gu.edu.au).
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| **AIHA** | **American Industrial Hygiene Association.** The largest Industrial Hygiene organisation in the world with over 13,000 members. They publish various books and the leading hygiene journal, the "*American Industrial Hygiene Association Journal*". Their web site is [http://www.aiha.org](http://www.aiha.org). |
| **AIOH** | **Australian Institute of Occupational Hygienists.** The professional body for occupational hygienists in Australia. |
| **Analytic Model** | Analytic models (c.f. Numeric models) of permeation permit the calculation of permeation rates and cumulative permeation by calculating the analytic solution to series expansions of partial differential equations describing the diffusion of chemicals through CPC. The limitations on their accuracy are the number of terms in the series expansion that are calculated and inherent limitations in the computation like rounding errors. All calculations are based on boundary conditions on the two surfaces of the CPC. |
| **ATR** | **Attenuated Total Reflectance.** A technique for determining the absorption spectrum of a material in contact with a transparent material, utilising the "evanescent wave" that decays exponentially into the "rarer" medium. The phenomenon is seen with glass, such as fish tanks, when total internal reflections will obscure a person on the other side but a fingerprint is visible if his finger touches the glass. The effective range of the technique in the infrared is about 2 μm with polymers (refractive index ~1.5). It effectively allows
otherwise opaque samples to be analysed. The technique is often coupled with FTIR as FTIR –ATR.

**BDT**  **Breakthrough Detection Time** (minutes). Time prior to the first appearance of the chemical on the inside of the CPC. BT is dependent on analytic method, sensitivity and how often measurements are made. ASTM F739 defines it as the time before the permeation is detected.

**BSP**  **British Standard Pipe.** Thread size commonly used in Australia for pipe fittings.

**BT**  **Breakthrough Time** (minutes). The time at which the permeant is first detected. For continuous measurements, this is the same as the BDT. It has sometimes been used interchangeably with Lag Time (LT).

**C**  **Concentration** of solvent at the surface of the test sample.

**Carrier Solvent**  The solvent used to dissolve the chemicals in a formulation.

**Closed Loop**  Closed Loop testing of CPC involves the collecting the flow past the "inside" surface of a CPC test sample. While it does permit the build-up of chemical on the inside of the sample, which may reduce the permeation rate of the test chemical, it does offer much greater sensitivity, particularly if the detector (e.g. PID, IR) does not affect the permeant. It is possible to change from closed loop until breakthrough is detected, then switch to open loop. When the test is performed with stain tubes it will give similar results to closed loop testing.

**Collecting medium**  A liquid or gas that does not affect the measured permeation an in which the test chemical is freely soluble or absorbed to a saturation concentration greater than 0.5 weight or volume percent (ASTM F739, 1996).

**Collecting Flow**  The flow of a fluid (gas or liquid) through the collecting volume of a two-chambered permeation cell.

**Collecting Flow Rate**  The flow rate of the collecting flow in mL min\(^{-1}\).

**Collecting Area**  See also exposed area. The area in cm\(^2\) of a test sample that is swept by the collecting flow, or exposed to a collecting fluid. In most cases the collecting area will be the same as the exposed area.
CPC **Chemical Protective Clothing.** This includes gloves, splash suits, chemical suits, boots and aprons.

**Cycle Frequency**  For intermittent exposure, the reciprocal of the Cycle Time.

**Cycle Time**  for Intermittent exposure is the sum of a wet time and a dry time.

**Diffusion**  The random movement of molecules. There will be an overall movement of molecules down a concentration gradient. The rate at which they move is characterised by their diffusion coefficient $D$ (cm$^2$min$^{-1}$). [This should not be confused with $D$ for dispersive forces, also used in this work for consistency with other published work.]

**DL**  **Detection Limit.** The analytic limit of detection. This is variously defined in terms of the ability of a system to detect permeation above a known zero background. In this work, the distribution of the background signal was found to be Normal, allowing the DL to be two standard deviations above the background signal to determined with a 95% certainty. In the context of this work, the DL refers to the minimum detectable permeation rate in $\mu$g cm$^{-2}$min$^{-1}$.

**Drain Time**  The short (~5 second) time to drain liquid chemical to the cell reservoir in an automated intermittent exposure permeation cell.

**Dry Time**  The period between successive Wet Times in an automated permeation cell, when the residual solvent is dried from the surface of the sample.

**Exposed Area**  The exposed area of a test sample is the region of the sample in contact with the test chemical. This is always somewhat smaller than the sample area for permeation cells, as the circumference of the sample is not exposed but used to clamp the sample in the cell.

**Effective Wet Time**  A term developed to compare intermittent exposure cell data with continuous exposure data with the same chemical-CPC combination. The cumulative exposures for the same test times are compared and the wet time scaled to give a cumulative exposure related to the total contact time. It is a crude method to account for the time the solvent takes to evaporate from the sample at the end of the wet time.

**FTIR**  **Fourier Transform Infrared.** An infrared spectroscopic technique using a mathematical transform of interference fringes of an infrared
absorption spectrum created by an interferometer. The technique is faster and more sensitive than dispersive instruments using diffraction gratings or prisms, and so lends itself to kinetic measurements such as permeation testing of CPC.

**Garment**
Any finished item of Chemical Protective Clothing, including gloves, chemical suits, aprons and boots

**GC**
**Gas Chromatograph.** An analytical instrument often used in permeation studies. The instrument offers sensitivity and the ability to measure mixtures of chemicals. It is coupled with a range of detectors as GC-FID, GC-MS and the like.

**GC-FID**
Gas Chromatography with a Flame Ionisation Detector.

**GC-MS**
Gas Chromatography with a Mass Spectrometer as a detector.

**Inside**
The "inside" surface of a CPC garment is the side towards the skin of the user. It is usual in permeation testing to expose the visible surface and measure permeant emerging from the side facing the skin.

**LT**
**Lag Time.** The intercept of the straight part of the integral or Closed Loop permeation curve with the time axis. It is less dependent on analytic detection limits than Breakthrough Time. It appears to have its origins with the mathematically derived "Time Lag" developed in polymer chemistry.

**Miran**
**Miniature Infrared Analyser (Foxboro).** A single beam 20 m pathlength, portable infra red analyser. Model 1 A (manual) and 1B (computerised) were used in the referred literature. It is severely affected by changes in water vapour and carbon dioxide levels and the large (~2 L) sample chamber limits rapid response of the meter, even at large (Lpm) flow rates.

**NATA**
**National Association of Testing Authorities.** The official organisation in Australia for certifying measurements.

**nBT**
**Normalised Breakthrough Time.** Usually 0.1 μg cm\(^{-2}\)min\(^{-1}\) for open loop testing and 0.25 μg cm\(^{-2}\)min\(^{-1}\) for closed loop testing. Developed to make BT estimates independent of the analytic sensitivity by specifying a detection limit. The toxicity of the chemical is not considered.
Normalised collection flow rate. The flow rate through the collection half of a two-chambered permeation cell expressed as a flow rate per unit exposed area of the test sample. As the amount of permeant through a test sample can be expected to be proportional to the exposed area of the sample, a given collecting flow rate allows concentrations of permeant in the effluent flow from different permeation cells to be similar.

Numeric Model Numeric models (c.f. Analytic models) of permeation permit the calculation of permeation rates and cumulative permeation by calculating the numeric solution to partial differential equations describing diffusion through CPC. The limitations on their accuracy are the formulation of the model, the number of layers that divide the thickness of the CPC and the time increment between successive calculations. There are also inherent limitations in the computation such as rounding errors. The boundary conditions on the surfaces of the CPC permit the calculation of complex concentration profiles through the CPC.

Open Loop Open Loop testing of CPC involves the single pass of the Collecting Flow past the "inside" surface of a CPC test sample to a detector. This approach is less likely to inhibit permeation by allowing the concentration on the "inside" surface of the test sample to rise. Compare with Closed Loop testing. Most solvent testing is Open Loop testing.

PC Personal Computer. The initial work developing the GloveTest rig was performed on a generic PC with a 486 SX processor, but this was upgraded to a faster Dell PC with a Pentium 133 processor and more memory and disk space.

Penetration The bulk movement of chemical through CPC by holes, tears, zips and other openings. Not to be confused with permeation.

Permeant The chemical used in testing CPC or the chemical as it emerges on the inside of a garment or test sample.

Permeation The molecular process of a chemical transported through CPC. The chemical adsorbed into the CPC, diffuses through it and then desorbs on the other side.
**Poisson ratio** An elastic constant characterising a material. The Poisson ratio is the ratio of the lateral contraction per unit breadth to the longitudinal extension per unit length when a piece of material is stretched. For steel the ratio is about 0.3, but for incompressible materials it is 0.5. Neoprene and rubber approach 0.5.

**PR** **Permeation Rate.** The flux of chemical though a membrane. The units are mass per unit area per unit time, usually $\mu g \, cm^{-2} \, min^{-1}$ for testing of CPC.

**Protection Factor** For a intermittent exposure for a given cycle and wet period, the ratio of the Cumulative Permeation with continuous exposure against the Cumulative Permeation with intermittent exposure.

**Reference Neoprene** 400 $\mu m$ neoprene sheet as referred to in ASTM F739, 1996 and available in small amounts from ASTM Committee F23.

**Repeat Time** The time between successive measurements on a given cell used in a permeation rig with multiple cells.

**S** **Solubility** ($g \, g^{-1}$) The amount of solvent that will dissolve in a CPC sample. It is sometimes expressed as $g \, cm^{-3}$ or $\mu g \, cm^{-3}$.

**Single-chambered permeation cell.** A permeation cell with a single section that contains the test chemical, but with no provision for a second section to contain a fluid (liquid or gas) to collect the permeant. The pressurised ATR permeation cell is a single-chambered permeation cell. See also two-chambered permeation cell.

**SD** Standard Deviation.

**SSPR** **Steady State Permeation Rate** ($\mu g \, cm^{-2} \, min^{-1}$). Test sample permeation rate rarely reaches a true steady state, but it is an indicator of the near constant permeation rate under continuous exposure to a chemical.

**Steady State Cyclic Permeation Rate.** The repeating permeation pattern that develops under cyclic intermittent exposure.

**STEL** **Short Term Exposure Limit.** For chemicals that have acute effects, a STEL of 15 minutes is sometimes given, to protect workers from these effects.

**TLV** **Threshold Limit Values.** Occupational exposure limits for physical and chemical agents in the workplace that are thought to protect most workers from adverse health effects, for a working lifetime
exposure to that agent. Some chemical agents have a "skin" notation to indicate that the skin may be a significant route of entry. The term is widely used, but registered by the ACGIH.

**TWA**  
*Time Weighted Average.* The average concentration of a chemical in air, calculated over a working day.

**Two-chambered permeation cell.** A permeation cell with a section that contains the test chemical and a section that contains a fluid (liquid or gas) to collect the permeant. The CPC sample under test divides the chambers. The ASTM F739 cell is a two-chambered permeation cell. See also single-chambered permeation cell.

**VBA**  
*Visual Basic for Applications.* A version of the Microsoft Visual Basic programming language packaged with the Microsoft Office suite of programs to write "macros".

**Wet Time**  
The short period used to wet a test sample with chemical in an automated intermittent exposure permeation cell. This comprises a succession of wet pulses followed by a period of draining of the solvent to a reservoir.

**Young's modulus**  
The ratio of longitudinal stress to longitudinal strain for a material under tension or compression.
CHAPTER 1. INTRODUCTION

SECTION 1.1 BACKGROUND TO THE RESEARCH

When chemical protective clothing (CPC) is ranked for use in the workplace, breakthrough times and steady state permeation rates are used. These parameters are derived from permeation testing the item against single pure chemicals using the ASTM F739 protocol (ASTM F739, 1996). While there is a large volume of basic data, there has been little explicit questioning of the methods of testing, particularly in relation to permeation cell designs, testing conditions and protocols.

Difficult-to-test chemicals have been generally ignored and there has been limited investigation of the methods for permeation testing of these chemicals.

In order to improve the relationship between testing procedures and workplace use, the ASTM F1383-1996 method for intermittent testing evolved, but as yet there is a paucity of research literature on the method itself and its application.

SECTION 1.2 CURRENT RESEARCH IN CHEMICAL PROTECTIVE CLOTHING

Permeation testing of Chemical Protective Clothing (CPC) became popular in the 1970's after publication of the 1974 US Occupational Safety and Health Administration standard for carcinogens (OSHA, 1974) requiring that garments used with thirteen carcinogens be "impervious". With this legislative interest in the US, there was an increase in research aimed at determining the barrier properties of CPC with a variety of pure chemicals and a limited number of mixtures and formulations.

An indicator of research activity in CPC is the annual number of articles published in the American Industrial Hygiene Association Journal (the principal journal for peer reviewed papers on CPC). Figure 1 shows the rise and fall of papers relating to CPC, smoothed with a moving five year average. The first paper in the occupational hygiene literature on permeation of CPC was by Weeks and Dean (1977), followed by a growing interest that peaked around 1988. There have been relatively few papers on CPC in the other international occupational hygiene journals.

Chapter 1. Introduction 1
Figure 1 Papers relating to CPC in the AIHA Journal

The peer reviewed "Performance of Protective Clothing" ASTM STP series (published) also provide a forum for the presentation of current research in the area.

Research in CPC has been classified into four main areas (Berardinelli, 1995) – test methods, decontamination, heat stress and toxic waste sites, though new areas like latex allergy have attracted some attention in the medical sciences (Katelaris et al., 1996; Berky et al., 1992), due to the widespread use of latex gloves in the medical, dental and biomedical sciences. The peer-reviewed proceedings of the Sixth International Symposium on the Performance of Protective Clothing (Stull and Schwope, 1997) grouped research as either the development of new procedures or the application of established procedures, for testing both materials and items of protective clothing. This work concentrates on innovative test methods and further develops the theoretical basis for approaches to measurement of permeation and the interpretation of results.

The dominant international influence on approaches to permeation testing of chemical protective clothing has been the US ASTM standards, in particular ASTM F739 "Standard Test Method for Resistance of Protective Clothing Materials to Permeation"
by Liquids or Gases Under Conditions of Continuous Contact" (ASTM F739, 1999a)\(^1\) in its various revisions from 1981. This standard specified a test cell, which many found difficult to use. The utility of the ASTM F739 cell was also limited by its design. These factors will be considered in detail below. A range of different test cells appeared in the occupational hygiene literature but there was only one instance of explicit cell design criteria being formulated (Schwope \textit{et al.}, 1988b). There have been a number of attempts to validate alternate cells against the standard ASTM cell (Patton \textit{et al.}, 1988; Vahdat, 1988; Henry III, 1988b).

Some researchers have examined factors affecting permeation, such as experiment temperature (Zellers and Sulewski, 1993) and sample thickness (Hassler, 1989; Schlatter and Miller, 1986). However, most work has concentrated on particular chemical-CPC combinations. Perkins has produced a number of papers investigating various aspects of CPC permeation and recent papers have addressed batch to batch variability (Perkins and Pool, 1997) and the effect of glove flexure on permeation (Perkins and Rainey, 1997). A recent paper on CPC permeation has examined the effects of flow rate on steady state permeation rates and the effects of submersion of a modified ASTM cell on temperature regulation of the experiment (Anna \textit{et al.}, 1998).

Though permeation indices have been used extensively by CPC researchers in reporting their results, there has been limited questioning of their appropriateness. Several papers have discussed permeation indices (Perkins, 1987b; Schwope \textit{et al.}, 1988; Leinster \textit{et al.}, 1986; Mellstrom, 1991a), however the sensitivity of these indices for ranking of CPC choices has not been investigated.

The testing of CPC under conditions of intermittent exposure has been codified in ASTM F1383 "Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Intermittent Contact" (ASTM F1383, 1996). Curiously, ASTM F1383-1996 was not preceded by peer reviewed publications on intermittent exposure and there appear to be no theoretical studies to predict the form of the cyclic intermittent permeation curves.

\footnote{The August 1999 version was brought to the attention of the author by one of the examiners. It appears identical to the 1996 version (ASTM F739, 1996) which will be referred to in this thesis.}
To overcome the difficulties associated with water insoluble or low vapour pressure chemicals, several approaches that required intimate contact between the test sample and a solid collection medium or a detector were tried. Thin sheets of silicon rubber were tried by Ehntholt et al. (1990) as a substitute for an aqueous or gaseous collecting medium. This approach was inherently limited, as it required the replacement of the rubber for each measurement. FTIR-ATR has been used to measure the permeation of mustard gas through CPC (Banerjee et al., 1995), but the method required special sample preparation that precludes this approach from routine use, or for testing laminated glove materials.

Developments in modelling of permeation through CPC have tended to be empirical with limited general applicability in the workplace (Perkins and Tippit, 1985; Hansen and Hansen, 1988; Goydan et al., 1992). More general models (Que Hee, 1996) still lack experimental verification and assume constant diffusion. More recently, chromatographic models have been successfully used to describe the permeation of mixtures of three chemicals but their general application has not yet been demonstrated (Lin and Que Hee, 1998). Developments in the understanding of diffusion through polymers may offer more generally applicable models of permeation, with diffusion coefficients that vary with chemical concentration (Neogi, 1996).

1.2.1 Current Gaps in Research

There is a need for a comprehensive set of design criteria for "ideal" permeation cells for testing CPC under conditions of continuous and intermittent exposure to overcome limitations in the standard ASTM F739 (ASTM F739, 1996) cell design. These include its large size, being fragile, inability to test solid chemicals, need for an excised sample, and its fragility. These will be discussed in the literature review. While there has been some study of the mixing of collecting flows in the ASTM cell (Anna et al., 1998), there have been no explicit attempts to design a cell that provides an “ideal” flow next to the test sample that efficiently removes permeant from the surface of the sample with little or no stagnation. The method of validation of permeation cells against the standard ASTM cell has had relatively little attention when the range of published cell designs is considered (Eiser, 1988; Henry III, 1988b; Lara et al., 1992b; Patton et al., 1988; Stull et al., 1992a; Vahdat, 1988; Mellstrom, 1991a; Mellstrom, 1991b).
The effects on permeation of collecting flow rate and flow patterns in permeation cells are not well understood. The effects of temperature on permeation have been extensively studied but the effects of pressure imbalance across the sample during testing require clarification. While commercial CPC garments will naturally tend to vary in thickness, the variability of test results in different test laboratories with standard test materials, such as the reference neoprene provided by Committee F23 of ASTM, must be determined to permit comparison of results from different laboratories. The method of measurement of the thickness of CPC samples has not been extensively examined, even though sample thickness is a critical parameter in evaluating the barrier properties of CPC.

The choice and application of permeation indices still requires attention and there is little information as to the uncertainties in the commonly used permeation indices.

Work with intermittent exposure cells is in its infancy and the methods of measurement and interpretation of permeation data requires detailed investigations.

Standard methods of measuring the permeation of CPC are not applicable to chemicals that are solids or have low vapour pressures and are water insoluble. While some researchers have made measurement with special cells (Fricker and Hardy, 1994) or techniques (Pinette et al., 1992f), simpler unattended methods that require little sample preparation are needed.

**SECTION 1.3 STATISTICAL APPROACHES**

Most statistical methods used in this work were simple tests to determine the appropriate size of samples with a nominal confidence limit of 95% and a power of 80%, or the calculation of confidence intervals for results. Appendix D outlines a method of determining sample size and a novel method for filtering spikes from instrument data to improve the analytic detection limit of permeation data.

**SECTION 1.4 OUTLINE OF THESIS**

The core of the thesis is the design of permeation cells, with explicit design criteria guiding the development of these cells. The work is divided into two major parts that each considers two-chambered permeation cell design, testing and mathematical modelling of permeation. The first part (Chapter 4 to 6) investigates two-chambered permeation cells for testing continuous exposure while the second part investigates...
develops and evaluates an automated permeation cell test system for intermittent exposure of CPC (Chapter 8 to 10).

At the interface of the two parts there is an additional chapter that considers a novel, single-chambered permeation cell for continuous exposure (Chapter 7).

1.4.1 The Scope of this Work

The selection and use of CPC in the workplace relies on good data from the permeation testing of the garments in the laboratory and an understanding of the limitations of this data. The methods and approaches to this testing are still evolving and this research becomes part of the process towards better test methods and an understanding of the permeation process and the permeation indices that are reported.

A hallmark of the ASTM F739 standard is an allowance to use alternate permeation cells but using a set test protocol. In this work, a permeation cell designed by the author was validated against the standard ASTM cell data using an innovative, computer controlled permeation test system (Chapter 3). The effects of operational parameters on permeation like collecting flow rates and flow patterns were investigated (Chapter 5 for continuous cells and Chapter 9 for Intermittent exposure cells). This assisted in the development of cell design criteria and gave a better understanding of the performance of the cell and interpretation of permeation data.

In Chapter 6, simple analytic solutions to a Fickian permeation model were implemented using a standard spreadsheet program to give a baseline for an intermittent exposure model and to investigate the applicability of modelling to experimental data from continuous cells. A numerical solution of the simple diffusion model was also constructed using a spreadsheet to predict the permeation of CPC under conditions of intermittent exposure and gain insights into how intermittent exposure affected the permeation of chemicals through CPC (Chapter 10). Concentration dependent diffusion was added to this numeric model to explain the shape of the permeation curves, though this gave little information on the permeation process.

Another permeation experiment involved the use of Fourier Transform Infrared (FTIR) spectroscopy (Chapter 7). FTIR is now a more affordable analytic tool that is becoming more common in occupational hygiene laboratories. The power and speed of FTIR, coupled with Attenuated Total Reflectance (ATR) permitted the development of a novel...
gas pressurised ATR permeation cell that has overcome many of the problems associated with permeation testing of water insoluble or low volatility chemicals. This included the specific ability to measure the permeation of solids.

Additional design criteria were developed for intermittent exposure cells using a similar approach to that used for continuous exposure. An automated intermittent exposure cell was constructed to satisfy these criteria (Chapter 8). Trials were performed to test the cell under different intermittent exposure patterns (Chapter 9).

1.4.2 Disciplinary Perspective

This work was performed from the disciplinary perspective of occupational (or industrial) hygiene, *the science and art of recognition, evaluation and control of health hazards in the workplace* (Clayton, 1973). As such, it relies heavily on the industrial hygiene literature, but touches on a number of other disciplines including the more fundamental sciences of physics, chemistry, and mathematics. Occupational hygiene gathers concepts from diverse disciplines and applies them to prevent occupational diseases and injuries.

Where a technique appears new to the field of occupational hygiene, more explanatory detail is given in the text rather than the appendices for the benefit of readers who are occupational hygienists.
CHAPTER 2. LITERATURE REVIEW

SECTION 2.1 PERMEATION AND PENETRATION

Initial interest in chemical protective clothing came from the medical profession. Surgical gloves were originally developed in 1890 for a US surgeon, William Halstead, to prevent dermatitis on the arms and hands of a surgical nurse caused by the surgical use of the antiseptic, mercuric chloride (Nuland, 1995). The protection afforded by these thin rubber gloves was adequate to prevent the dermatitis.

The founder of occupational medicine in the US, Alice Hamilton (Hamilton, 1925), was one of the first to recognise that the degree of protection afforded by CPC is finite and that the use of CPC may have a net detrimental effect.

"The consensus of opinion among men experienced in such industries as the production of coal tar intermediates, where skin absorption is of prime importance, seems to be against gloves as a protection. Gloves make the hands sweat and the skin soft and hot and in excellent condition for the absorption of poisons, and if there is even a small rip or tear in the glove letting the dust or liquid in, it will form what is practically a poultice of poison around the hand"

Skin exposure must follow the penetration of chemicals through holes in gloves. An appreciation of the subtler role of permeation - a molecular process involving the diffusion of chemicals though intact CPC had to wait nearly 50 years.

Pegum and Medhurst (1971) observed that areas of contact dermatitis on the hand of an orthopaedic surgeon corresponded to the use of self-setting bone cement made of a powder and a liquid monomer. Patch testing of the person by placing the chemicals inside excised fingers of the rubber surgical glove established that the agent permeating the glove was the methylmethacrylate monomer and more weakly, the 2.5% benzoyl peroxide in the polymer powder. This method effectively used the skin as a sensitive biological detector of permeation.

The permeation of the monomer (Pegum and Medhurst called it penetration) through a glove was demonstrated by placing the polymer powder in a sealed finger of the glove in a flask of monomer. The powder set, demonstrating the diffusion of the monomer...
through the glove into the powder. Tests were also performed with domestic rubber gloves and PVC gloves and it was recognised that their greater thickness afforded better protection for the use of bone cement.

This appears to be one of the first systematic investigations of glove permeation by chemicals and the reporting of health effects from such exposure. This work was reported in an early article (Sansone and Tewari, 1978) on glove permeation in the American Industrial Hygiene Association Journal. Pegum and Medhurst (1971) stated that these effects were “an unexpected finding”.

SECTION 2.2 HISTORICAL METHODS OF MEASURING PERMEATION

The findings that diffusion through a polymer membrane can occur, should not have been "unexpected", as the diffusion of chemicals through intact rubber membranes was well described 170 years ago, by Thomas Graham (1829)

Fick's First Law (Crank, 1975) states that the amount of chemical permeating a membrane depends on the concentration gradient across the membrane and the diffusion coefficient of the chemical in the membrane. Fick's Second Law states that the rate of change of concentration depends on the flux gradient.

\[ F = -D \frac{\partial C}{\partial x} \]

.................................Equation 1 Fick's First Law

and

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

................................. Equation 2 Fick's Second Law

where

- \( F \) flux of chemicals through the membrane (mg cm\(^{-2}\)),
- \( D \) diffusion coefficient (cm\(^{-2}\) min\(^{-1}\)),
- \( x \) distance into the membrane (cm),
- \( C \) concentration (mg m\(^{-3}\)) at \( x \), and
- \( t \) time (min).
This understanding of the diffusion process underlies testing and modelling chemical permeation through CPC.

**SECTION 2.3 METHODS OF MEASUREMENT OF CPC PERMEATION**

The most widely adopted chemical permeation testing standard for CPC, ASTM F739-1996 (ASTM F739, 1996) considers permeation to occur in three stages -

1. **Sorption of molecules of the chemical into the contacted (outside) surface of the material**
2. **Diffusion of the sorbed molecules in the material; and**
3. **Desorption of the molecules from the opposite (inside surface of the material into the collecting medium.**

Measurement of permeation thus largely equates to measurements of diffusion of which Cussler (1984) said -

"measurements of diffusion are a Holy Grail requiring noble knights who dedicate their lives to the quest".

Consequently there are many methods of measuring diffusion, of which some are applicable to CPC. Discussion is restricted to these.

The most widely accepted method of permeation testing ASTM (ASTM F739, 1996) measures the concentration of permeant on the inside of a CPC garment. From the sample area and the collecting volume or the collecting flow rate, the chemical flux is calculated. This method permits a comparison of choices of CPC, but does not give direct information on the interaction of the test chemicals with the CPC polymer. This flux of chemical determines the dermal chemical exposure of a worker. Permeation testing is the method used in most of this research.

An alternative method, measuring the mass of challenge chemical in the CPC matrix by immersing a test swatch in the test chemical (Crank, 1975), gives more direct information on the interaction between the challenge chemicals and the polymer. The weight of the swatch is determined by the "pat and weigh" method. Here the swatch is patted dry before quickly weighing it and then returning it to the jar of chemical. The weight gain with time is recorded. This method gives a direct measure of the average
concentration of the test chemical in the polymer matrix. However, it gives limited information about the permeation rate through the CPC.

Two types of test chemical–polymer interaction illustrate the limitations of each method.

- In the first case, if a polymer swells with the test chemical, then the amount of chemical in the polymer matrix will change significantly with time, but this change will not directly relate to the permeation rate through the polymer. This is a bit like a sponge soaking up water. Weight gains would only allow ranking of protective properties of polymers with similar internal structures for molecular diffusion.

- In the second case, if there are strong forces between the polymer chains, and the polymer is very polar, then a high permeation rate with a polar solvent could be expected with little swelling of the polymer. (In the extreme case, an open mesh would give low weight gain but give no permeation protection.) Simple theory involving weight gains fails to predict the permeation rate through the polymer.

Ideally, both the permeation rate through the polymer and information on the interaction of the test chemical with the CPC polymer would be available to guide CPC selection and use.

Sophisticated methods using X-rays and nuclear magnetic resonance have been used in polymer research (Fieldson and Barbari, 1995; Neogi, 1996; Elabd et al., 1997) to measure concentration gradients of chemicals inside polymer membranes. These methods do not lend themselves to routine measurements of permeation through CPC, and will not be further discussed.

**SECTION 2.4 TESTING AND WORKPLACE CHEMICAL EXPOSURES**

CPC is used as a barrier between chemicals in the workplace and the skin (Grandjean, 1990). If the toxicity of a chemical is related to the cumulative amount absorbed during a working day, then the cumulative amount of chemical permeating the CPC will be a key indicator of toxic dose.

The effects may be local or systemic (Jacobs, 1990), acute or chronic or subchronic (Hobson, 1993). Permeation through CPC begins at imperceptible levels and often increases to a quasi-steady state level, at a rate dependent on the diffusivity and the
solubility of the chemical in the CPC (Nelson et al., 1981). For many chemicals, permeation is detected inside the CPC within minutes (Johnson, 1990) and the chemical dose is largely a function of wear times, particularly if the chemical lacks warning properties like irritation of the skin. In particular, for very toxic chemicals, permeation may occur below the normal analytic limits of detection (Ursin and Drabaek, 1988). Reducing the collecting flow rate to increase analytic sensitivity may lead to underestimating the open loop permeation rate (Anna et al., 1998), leave inadequate flow to the detector, or make the response of the measurement system sluggish.

It is necessary to relate the permeation testing of CPC to the exposures they are supposed to prevent. The relevance of the test data to decisions on the selection and use of CPC can be answered in part by an examination of the route of chemicals to the skin and some of the variables that affect dermal exposure.

2.4.1 Routes of Transport of Chemicals to the Skin

The skin is a complex bio-membrane with varying thickness, hydrophilic and hydrophobic properties, and variations such as that of blood supply and the degree of hydration due to sweating (Grandjean, 1990; Fiserova-Bergerova, 1993; Jacobs, 1990).

Some CPC will fit closely, literally "like a glove", for performing tactile tasks. Others, like aprons, may be in loose connection to the body. Chemical suits and gloves supported by fabric will vary in the contact they make with the skin, but the atmosphere inside the garments will be essentially closed and allow temperature and moisture to rapidly rise. Within a couple minutes of donning a supported glove, it is easy to show that the temperature inside the glove will rise from a normal skin temperature of around 25°C, to around 36°C (Unpublished data, Bromwich, 1997). Sweating commences and the skin rapidly hydrates (Grandjean, 1990).

On initial exposure of a CPC garment to a chemical, the chemical may reach the skin by several routes after first permeating the garment. It may partition between the CPC and the atmosphere inside the glove (Grandjean, 1990) and come in contact with the skin as a vapour; dissolve in sweat and come in contact with the skin in solution; or partition directly between the garment and the skin during periods of contact. The relative importance of each route and combinations of routes would depend on a variety of factors, but the properties of the permeating chemical could be expected to dominate the uptake into the skin. Figure 2 is a pictorial representation of the routes from the CPC to
the skin by Yang and Li (1996) involving transport of the chemical as a vapour, liquid or solid to the skin. Direct transfer from the CPC to the skin by rubbing between the skin and CPC was demonstrated. The more traditional model of skin exposure though CPC assumes only desorption into the air inside the CPC garment (Schwope, 1986).

![Transport routes from CPC to the skin](image)

**Figure 2 Transport routes from CPC to the skin**

Chemical that have a low vapour pressure like furfural or that dissolve easily in water like methanol may condense on the skin (Fiserova-Bergerova, 1993).^2^  

### 2.4.2 Variables Affecting Dermal Exposure

During a task, a glove will be subject to a complex pattern of flexing, stretching and shear forces that not only thins the material, but also may affect its permeability. With dipped gloves, the thickness of the glove will also vary over its surface to varying degrees depending on the method and quality of manufacture. If the glove is exposed to a chemical formulation, then the exposure pattern will not be even over the surface and the composition of the mixture will change as different components evaporate at different rates.

Thus, the variables affecting the skin exposure and health of a person wearing CPC in the workplace will include:

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^2^ The author has noted the potential for mercury vapour dissolving in sweat on the arm and running down into a glove (Bromwich D W, unpublished observations in a gold room). The contribution of this component is unknown, but the hydration of the skin inside the CPC reduces the barrier properties of the *stratum corneum* and would facilitate uptake of the chemicals in the sweat. The barrier properties of the CPC may be effectively short-circuited by this route.
• **Polymer formulation**, including the polymer mix and plasticisers, fillers and method and quality of manufacture, and batch variations (Perkins, 1990b);

• **Challenge chemical formulation** where the interaction of one component of a formulation or mixture with the CPC polymer can facilitate the permeation of another (sometimes more toxic) component (Nelson *et al.*, 1981; Eiser, 1988; Forsberg and Faniadis, 1986; Khan *et al.*, 1997);

• **CPC thickness**, which varies due to manufacturing methods and is compromised by seams, openings and microscopic defects (Dimit *et al.*, 1992; Berardinelli and Hall, 1985; Bromwich *et al.*, 1997; *Jencen and Hardy, 1989*);

• **Exposure pattern**, with an expectation that regions of CPC with greater contact with chemicals will contribute relatively more than uncontaminated regions (Berardinelli and Hall, 1985; Bromwich *et al.*, 1997);

• **Temperature** of test sample and surrounds, and temperature gradients (Billing Jr and Bentz, 1988; Zellers and Sulewski, 1993; Perkins and You, 1992; Anna *et al.*, 1998);

• **Initial state of the garment**, history of use including prior decontamination and laundering (Forsberg and Faniadis, 1986; Vahdat and Delaney, 1989; Perkins, 1991; Schlatter, 1990);

• **Mechanical effects** including mechanical forces, cuts and abrasion (Williams, 1979; Eiser, 1988; Canning, 1997; Perkins and Rainey, 1997);

• **Individual variability** in skin properties such as the toxic response of an individual to direct effects of a chemical, systemic effects (Emmett, 1991; Thomas, 1991; Pirot *et al.*, 1997; Grandjean, 1990), and effects like latex allergy to the CPC itself (Walls, 1996).

It would be difficult, if not impossible, to address all of these variables to give a comprehensive suite of information to guide the selection and appropriate use of CPC. Crude methods, using laboratory testing of samples under standardised conditions, are necessary to permit the basic ranking of choices of CPC. One of the most important considerations is the design of the permeation test cell, as it needs to not only simulate the practical CPC situation as closely as possible, in addition to being adaptable to a large range of test CPC samples and chemicals. It is also desirable that the test cell be standardised, though standardisation can inhibit design improvements. The ability to link to historical data sets through calibration factors or demonstrated equivalence of test methods under standardised conditions may be more important.
SECTION 2.5 PERMEATION INDICES

Permeation indices will now be considered in more detail, as they are the most significant outcome of permeation testing.

To be able to rank selections of CPC with a particular chemical, a number of indices have been developed, for example to quantify the first discernible appearance of permeant and amount of permeant, either as a permeation rate or total amount permeating in a certain time. The most common are those required in the standards – Breakthrough Detection Time (BDT), Normalised Breakthrough Time (nBT) and Steady State Permeation Rate (SSPR) in ASTM F739-1996 and Lag Time (LT) and Cumulative Permeation (CP) in the 1988 draft ISO standard (Mellstrom, 1991a).

These indices could be used in the ranking of chemical protective clothing to guide their selection and use and to establish "safe" wear times. Whatever the indices, the early researchers (Williams, 1979) realised that testing performed in laboratories could not emulate workplace performance of CPC. There are no specific indices for intermittent exposure patterns.

There has been a gradual evolution from determining these indices from a chart recorder output of a permeation curve to calculated indices using statistical tools as a result of the introduction of computers to log the data (Jencen and Hardy, 1988). With the data in a digital form, post processing of the data is relatively easy.

As the first performance requirements for CPC were for "impermeable" garments, it was natural that the first indices should be an indication of lack of impermeability. In its simplest form these were breakthrough times.

2.5.1 Breakthrough Times (BT's)

There are a number of different ways of determining a time corresponding to the first appearance of a permeant through an item of CPC. The most accepted are Breakthrough Detection Time (BDT), nBT and LT. However, Fick's Second Law (see Section 2.2) implies that only at time zero is there zero concentration on the inside surface of a sample. This had been verified with radioisotopes (Ursin and Drabaek, 1988) using $^{14}$C nitrobenzene with neoprene (BT 2 seconds), and $^{14}$C acetone with Viton-chlorobutyl laminate (BT 2 minutes, vs 54 minutes with GC).
In practice, the detection of breakthrough of a chemical is largely determined by the sensitivity of the chemical detector. The noise associated with the detector signal also affects the minimum detectable permeation rate.

As previously noted, Williams (1979) ranked CPC using the ratio of BT to SSPR with some success. Leinster et al. (1986) standardised the approach to estimating the BT with a choice of either estimating the BT at a predetermined permeation rate (1 \( \mu g \) cm\(^{-2}\) min\(^{-1}\) was suggested) or by drawing a tangent at the inflection point (close to the value at half the SSPR) on a permeation curve to meet the time axis. This approach removes much of the problem associated with comparing results from estimates of BT with instruments of differing sensitivity however, it has not been used by others.

As the art developed, Schwope et al. (1988) produced the first major review of the field. The scaling of Lag Time with the square of the thickness of the CPC was confirmed. They showed that BT could be calculated for a given detection limit, but that other researchers often erroneously assumed a squared relationship between sample thickness and BT, as BT and LT were seen as almost synonymous.

A statistical approach to BT was taken by Jencen and Hardy (1988), who calculated BT as the time when the detector response rose by three standard deviations above the noise for the trial. There is continued confusion as to how to calculate BT – whether to use two or three standard deviations of a "background" noise signal to determine BT.

**Breakthrough Detection Time (BDT)**

As most measurements of permeation are performed at intervals using instruments like gas chromatographs, Breakthrough Detection Time (BDT) has been defined in ASTM F739-1996 as

"the elapsed time measured from the start of the test to the sampling time that immediately precedes the sampling time at which the test chemical is first detected"

The unstated disadvantage of this index is that it can be unduly conservative, as measurements at large intervals will tend to place a low value on the BDT. When carcinogens with no known safe level of exposure are being tested, BDT is the most
conservative index available to minimise exposure. However, even well measured BT’s will not give a quantitative estimate of exposure, but only help rank choices.

**Normalised Breakthrough Time (nBT)**

To permit data to be compared between laboratories, BT’s at the same permeation rate must be compared or the less sensitive measurement will indicate a longer BT. This was codified in ASTM F739-1996 at 0.1 μg cm⁻²min⁻¹ for open loop testing and 0.25 μg cm⁻²min⁻¹ for closed loop testing as a Normalised Breakthrough Time (nBT). This does require that the analytic detection limit be known, particularly if nBT is to be used to compare cells with the ASTM cell.

The method of determining the detection of 0.1 μg cm⁻²min⁻¹ to estimate the nBT in ASTM F739-1996 is stated as “*twice the baseline noise level of the system with the blank cell in place*”. This is open to interpretation, as the method of determining the noise level is not defined. Appendix X2 of the standard outlines a method of slowly injecting solvent into the collecting side of a cell that has an aluminium blank as the test sample. This appears to be based on a paper by Verschoor *et al.* (1988) who used a semi-quantitative estimate of the noise level from a chart recording of the permeation rate, and dilution of the test chemical with an undetectable chemical to achieve low injection rates. The method does not directly relate to the detection of breakthrough under test conditions, as the test sample is substituted by an aluminium blank. If the sample itself produces any volatile contamination, then this would adversely affect the detection limit.

The International Union of Pure and Applied Chemists (IUPAC) and the American Chemical Society Subcommittee on Environmental and Analytical Chemistry (Long and Winefordner, 1983) both suggest a statistically based detection limit. A detection limit of three standard deviations (SD) above the blank is suggested, particularly if the scatter of measurements of the blank are not normally distributed. In this experiment it was found that the distribution of the noise signal about the blank signal approximated a normal distribution, so two rather than three SD above the blank would give a confidence level of 97.7% that a non-zero permeation rate was detected. This compares with a lower 89% confidence level when the blank distribution is not known, requiring three SD rather than two SD, to be used.
Normalised breakthrough time lacks a direct toxicological meaning as an index of CPC performance as the toxicity of different chemicals varies. While its use does allow comparison of data, it must be treated with caution as significant amounts of toxic chemical may permeate before the nBT is measured. Ursin et al. (1995) claimed that “even extremely small amounts of particularly toxic solvents can affect DNA synthesis”.

**Lag Time (LT)**

The origin of Lag Time is given in detailed history of transport of gases through membranes by Stannett (1978). In 1920, Daynes had found that the steady state behaviour of the membrane could be used to determine the diffusion coefficient "D" using the "Time Lag" (Lag Time) time intersection of the asymptote of the cumulative permeation. Figure 3 below illustrates the concept, using axes scaled to make them dimensionless.

![Figure 3 Cumulative permeation curve and Lag Time](image)

Mathematically, this was expressed as a relationship between the Lag Time "LT", the membrane thickness "l" (cm, “L” in Figure 3 ) and the diffusion coefficient "D".

\[ LT = \frac{l^2}{6D} \text{ (minutes)} \]

\[ \text{Equation 3 Lag Time} \]

The derivation of this relationship is given in standard texts, for example Crank (1975).

The steady state permeation rate or permeability "P" allowed the determination of the product of \( D \) (cm\(^2\) min\(^{-1}\)) and solubility "S" (g g\(^{-1}\)) per unit thickness \( l \).
\[ P = D \frac{S}{l} \text{ (\(\mu g\) cm}^{-2}\text{ min}^{-1}) \]

........................................ Equation 4 Permeability

Daynes realised that he could thus determine both "D" and "S". This ability to relate Lag Time to the diffusion coefficient has lead to some support for its more recent use, particularly by Perkins (1987b).

Lag Time has no direct physical significance, but as it is derived from an asymptotic line, it can be measured far more precisely than a breakthrough time derived from detection limits. As the Lag Time is similar to the BT, it has the potential to be used as a more accurate method to rank choices of CPC.

As the terminology matured, it could be expected that the meaning of the terms would become more precise. Lag Time and BT's have been used interchangeably in many papers. Stull and Pinette (1990a), perhaps inadvertently, also used Lag Time to refer to the time taken to reach steady state conditions, called Steady State Time (SST) by Fricker (1992).

Perkins et al. (1986b) reported Lag Time with BT and pointed out (Perkins, 1987b) that unlike BT, Lag Time would be "constant from one test to another regardless of detection limits". However, Schwope et al. (1988) showed that Lag Time still had some dependence on detection limits. In more recent work Perkins (Perkins and Pool, 1997) did not reported Lag Time data. Perhaps the adoption of nBT for comparison of BT data has made LT estimates less important.

2.5.2 Permeation Rates
Both steady state and cumulative permeation will now be examined.

**Steady State Permeation Rate (SSPR)**
As chemical permeates through the CPC, the concentration gradients tend to settle to a linear gradient across the sample and the permeation rate settles to a constant. Nelson et al. (1981) showed that not all permeation curves through CPC result in a true steady state permeation rate occurring. In these cases the maximum value is sometimes taken.

Jencen and Hardy (1988) used a Steady State Time (SST) derived by calculating the time when one standard deviation below the SSPR intercepted the permeation curve.
This approach would tend to give precise, reproducible results, but has not been adopted by others. The SST is not directly applicable to the workplace.

**Cumulative Permeation (CP)**

Leinster *et al.* (1986) suggested the use of cumulative permeation values at 30 and 60 minutes, and the concept is supported by Goydan *et al.* (1988a), who also defined a BT based on a predetermined cumulative permeation of chemical, but noted that a toxic amount may have accumulated before the BT was reached as BT times tend to be standardised for a set permeation rate, often 0.1 μg/cm²/min (ASTM-F739, 1996). The problems in linking BT to dermal toxicity are discussed below.

Cumulative Permeation may be adopted in a new International Draft Standard, ISO 6529 (ISO/DIS 6529 (Draft), 1998), calculated at "four times equally spaced over the duration of the test and the average of the three values of cumulative permeation for each time for each data set". If adopted, this approach will make comparisons of data from different laboratories difficult, as the reported test times vary. It would be desirable to specify set times for determining cumulative permeation.

Ideally, cumulative indices should be able to relate the dermal (and systemic) toxicity of the material to the amount of chemical reaching the skin during a task. However, this is not generally possible, as thresholds for health effects vary for different chemicals, sensitivity to chemicals may vary widely over the skin, and further, the chemical may affect distant organs, like the liver (Emmett, 1991; Grandjean, 1990).

The linking of permeation of chemicals through CPC to dermal toxicity (local and as a route of exposure for systemic toxicity) has been attempted. For instance, Eggestad and Johnsen (1989) defined breakthrough of fabrics (using a special chemical penetration cell) in terms of dermal toxicity of the test chemical. For mustard gas they used cumulative permeation of 4 μg cm⁻² to determine significant breakthrough as this was considered the lowest concentration that would cause damage to human skin. Other work by Schoene *et al.* (1989) using a gas exposure cell indicated a much lower threshold effect for mustard gas (0.1 to 1.1 μg cm⁻²) using rabbits ears, indicating that absolute figures using a toxicology based criteria could be challenged. Experimental methods, species differences and assessment criteria may account for some of the difference, as would the skin location (Emmett, 1991), but the difference is still over an order of magnitude. Finally, there is no standard skin for testing. The American
Conference of Governmental Industrial Hygienists (ACGIH, 1999) recognises the skin as a route of exposure in the setting of airborne exposure limits for chemicals, through there has been some (Fiserova-Bergerova, 1993; Kennedy Jr et al., 1993) examination of this route and criticism of the range of chemicals annotated to indicate possible dermal exposure.

2.5.3 Application of Indices
While breakthrough times give an indication of the first measured permeation through CPC, permeation rates quantify the amount permeating. To be practicable in the workplace, a single index was needed to rank selections.

This was done by Forsberg and Keith (1995) in their "Chemical Protective Clothing Permeation and Degradation Compendium" and in the electronic version, "GlovES". Here, ranges of published BT's (in minutes) were combined with permeation rate (in mg cm$^{-2}$min$^{-1}$) and given a ranking from zero to five. A long BT and low SSPR was given the lowest score to guide the best choice, so a ranking of zero was best and five was unacceptable. Their decision matrix is shown in Table 1.

<table>
<thead>
<tr>
<th>Permeation rates (mg cm$^{-2}$min$^{-1}$)</th>
<th>Breakthrough Times (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>1 to 14</td>
</tr>
<tr>
<td></td>
<td>15 to 59</td>
</tr>
<tr>
<td></td>
<td>60 to 239</td>
</tr>
<tr>
<td></td>
<td>240+</td>
</tr>
<tr>
<td>&lt;1</td>
<td>4</td>
</tr>
<tr>
<td>1 to &lt;10</td>
<td>3</td>
</tr>
<tr>
<td>10 to &lt;100</td>
<td>4</td>
</tr>
<tr>
<td>100 to &lt;1000</td>
<td>5</td>
</tr>
<tr>
<td>1,000 to &lt;10,000</td>
<td>5</td>
</tr>
<tr>
<td>10,000 or greater</td>
<td>5</td>
</tr>
</tbody>
</table>

This method allows some flexibility with selection for different task times, but there would be uncertainties with some data due to varying testing methodologies.

Cumulative permeation may more directly relate to toxic effects, but it has not gained popularity as there are almost no cumulative permeation data.

SECTION 2.6 THE EVOLUTION OF PERMEATION TESTING OF CPC
It appears that much of the early research into the performance of CPC was not published in the peer reviewed occupational hygiene literature, but in internal reports and unpublished papers. This was acknowledged by Weeks and Dean (1977), who noted
“quantitative data concerning glove permeability is not readily available in the open literature”. Weeks and Dean's work was driven by the new regulatory requirements in the US to demonstrate that CPC used with carcinogens were "impervious".

An early paper that investigated chemical permeation through CPC was noted in a PhD thesis by Cvejanovich (1989). Cvejanovich referred to the work of (Calingaert and Shapiro, 1948) Calingaert and Shapiro (1948), who performed semi-quantitative investigations of the permeability of gloves by tetraethyl lead and ethylene dibromide. No other references to this work were found, and Cvejanovich noted the gap in research until the mid 1970's.

Interestingly, there appears to be more scientific rigour in some of the early papers where the standards of publishing analytic chemistry appear to have been applied. Later papers tended to follow a simple codified approach relating to the new glove permeation standards.

The utility of a permeation cell – the ability of a cell to test samples of CPC material or intact CPC garments with a wide range of test chemicals and using a wide range of chemical sensors, depends on the design and construction of the cell. Factors such as the construction material can affect more than one feature – glass construction may give good chemical resistance and permit the test sample to be observed, but it makes the cell fragile.

Weeks and Dean (1977) used a cell that looked very much a prototype of the standard ASTM cell that was to follow.
The cell design was primitive as no attention was paid to circulation of the collecting media and clamping was by paper clips. Later cell designs paid more attention to clamping cell halves together, though internal flow problems were not well addressed by any cell design that followed. Breakthrough Time (BT) was defined as

"that value obtained by extrapolation of the saline amine concentration vs time curve to a point where $A = (0.0000 + 2\sigma_{I,0})$"

This definition was more in accord with the accepted definition of Lag Time (as the time intercept of the closed loop or cumulative permeation curve), as the saline collecting media made the concentration cumulative, or "Closed Loop".

There were some methodological problems in the paper by Weeks and Dean (1970). Detection limits were considered, but it appears that there was an unstated assumption that the distribution of background measurements was Normal, as two standard deviations above the background was taken as the 95% confidence level that permeation was detected. It could be expected that this would be valid for many detectors where the noise for zero measurements varies randomly about zero. If the distribution had not been Normal, then the use of three standard deviations would have been more appropriate (Long and Winefordner, 1983), and would have given a higher detection limit. Weeks and Dean (1970) calculated diffusion rates by simply dividing the square of the thickness ($l^2$) by the "Breakthrough Time", so the Diffusion Coefficient ($D$) would have been overestimated by a factor of six as $D$ is commonly given (Crank, 1975) as

$$LT = \frac{I^2}{6D}$$

.............................................Equation 5 Lag Time
The regulatory push in the US to demonstrate CPC material "impervious" to carcinogens lead to BT's but not Permeation Rates (PR's), being reported. The trend towards a more comprehensive reporting of permeation indices was to follow.

A paper by Sansone and Tewari (1978) investigating CPC and carcinogens followed the next year. This paper was significant in that it started to put the understanding of permeation on a firm theoretical basis and recognised existing work outside occupational health and safety, including the often quoted work by Crank and Park, "Diffusion in Polymers" (1968).

Sansone and Tewari used a much smaller permeation cell, to limit the volume of carcinogenic chemical being tested, but the cell still used an aqueous collection media in a closed loop. In the absence of a specific testing standard for CPC, an ASTM standard for "Vulcanised Rubber or Synthetic Elastomers to Volatile Liquids" was used for guidance. Glove thickness and the difference between single and double layers was investigated. The difference between room temperature testing (21°C) and the skin temperature (35°C) was also noted, though a 35°C skin temperature would only be found in hot environments or inside a glove.

A polymer chemistry technique useful for determining phase changes in the polymer, Differential Scanning Colorimetry (DSC) was also mentioned by Sansone and Tewari (1980). This technique was used by the author’s group (Bromwich et al., 1997), and Perkins and Rainey (1997) to examine changes in the CPC polymer, but there has been little application of the technique to elucidate mechanisms of permeation of CPC.

Sansone and Tewari (1980) followed this paper with work on benzene vapour with a different cell design. The glove sample was supported with a steel mesh, but the flow patterns relied upon central orifices to collect the permeant. The collecting flow pattern appears indeterminate and the steel mesh may have trapped a thicker boundary of permeant next to the inside surface of the test sample, leading to an underestimation of the real permeation rate.
A concentration dependence of vapour permeation was demonstrated. A difference of one million was found with benzene vapour permeation of rubber at 10 ppm compared with saturated vapour. When corrected for concentration, the differences were attributed to a factor of 10 in the diffusion coefficient "D" and a factor of 20 in the solubility "S".

A year later Williams (1979) advanced the technology of permeation testing of CPC and the quality of reporting of results. A new cell was used, looking remarkably like the eventual ISO cell (Mellstrom, 1991a), which used gas as a collection medium rather than a static reservoir of water. Little attention was given to gas flow patterns or dead volume on the collecting side of the cell but the cell halves were securely clamped.

The cell was made of stainless steel and the sample was held in a horizontal position. Williams assumed that adequate protection was given by CPC before breakthrough (as a Lag Time) was detected. Permeation rates ($\mu g$ cm$^{-2}$min$^{-1}$) were also tabulated. The amount of chemical covering the sample was shown to have no effect on permeation.
Williams also observed the leaching of glove additives using gas chromatography, used stain tubes as an integrating detector, and tested eight cells sequentially with a multi-port valve on a thermal conductivity detector.

Variations were noted between similar gloves from different manufacturers (BT varied by a factor of 3). Williams also realised that the total amount of chemical permeating in a given time was important, and that the laboratory testing on new gloves, with neat chemicals at 21°C did not represent workplace usage. Some reuse trials were performed after the glove specimens were "allowed to stand until all traces of chemical were gone". How the absence of chemicals in the samples was determined before re-testing was not stated, but it is presumed that measurements were made until background levels were achieved. Williams (1980) modified his cell to be held by a clamp to permit the testing of intact garments.

![Figure 7 Williams' cell, showing intact garment testing (1980)](image)

The backpressure on the sample due to collecting flow of gas was balanced by the depth of the test chemical. The clamping force was made repeatable with a torque screwdriver, but the clamping force would be difficult to replicate, as the pitch of the screw thread was not given. All other researchers reporting torques on clamping bolts have also not reported the thread pitch. An additional permeation index, the time to reach half the Steady State Permeation Rate (SSPR), was introduced.

Williams (1981) extended this work with a different method using whole garment testing of gloves.
Though this method had the advantage that it tested the whole garment, in many workplace exposures the chemical exposure could be expected to be greater on the palms and fingers than the cuff. The permeation rate through dipped gloves is known to vary over its surface (Berardinelli and Hall, 1985; Bromwich et al., 1997), with the greatest permeation through the thinnest parts (the cuff) and the least through the thickest part (fingertips). Williams whole glove method would tend to overestimate the permeation rate and underestimate the BT found with real use. For suits or gloves manufactured from sheets of polymer of uniform thickness, the method may be more appropriate.

Tests on excised samples from gloves enabled Williams to rank gloves using the ratio of BT to SSPR, the highest number being the most desirable. Good agreement was obtained between rankings of gloves by patch testing and whole glove permeation measurements. The greater ease of testing glove samples rather than whole gloves has meant that whole glove testing has not been routinely adopted. Williams recommended whole boot testing, as the fabrication of boots was less uniform and testing with excised samples did not reflect the workplace protection afforded by boots.

ASTM Committee F23 was formed in October 1977 (Henry III, 1988a) and the ASTM F739 method was published in 1981 and revised in 1985, 1991 and 1996 (ASTM F739, 1996). These developments were reflected in the occupational hygiene literature, with the first formalisation of CPC permeation testing protocols by Henry and Schlatter (1981) and the publication of the ASTM cell design for use with a liquid collection medium.
The move towards codification of CPC testing meant that the growing body of test data could be made comparable, but the negative side was that the method of testing was less likely to be questioned. The testing outlined by Henry and Schlatter (1981) required the use of a sample with a large (78 mm) diameter and for the cell to be made of glass. The cell was suitable for use with liquids and gases as challenge and collection media, and the circulation of liquid challenge chemicals was resolved with the addition of a stirrer for the liquid version of the cell. It has the advantages that the cell is chemical resistant and that the sample is visible, thus allowing observations of degradation. However, the cell has a large collecting volume, necessitating a large amount of test chemical and multiple bolts are required to clamp it, resulting in slow and potentially uneven sample clamping.

The need for inter-laboratory test data was also noted by Henry. The ASTM cell in Figure 9 can be seen to be similar to that of Weeks and Dean's 1977 cell (Figure 4), but with the clamping flange of Williams' 1979 cell (Figure 6). In the open loop version of the ASTM cell (not pictured, ASTM F739, 1996), where the collecting and challenge halves are small, the collecting medium is directed towards the test sample, though the efficacy of removing permanent must be in doubt, as the flow rates recommended by ASTM F739-1996 underestimated the true permeation rate Anna et al. (1998). No design criteria for this cell have been published, but the cell was adopted by ASTM and continues to be the standard test cell, with international acceptance.

Nelson et al. (1981) appear to have been working in parallel with other researchers as evidenced by references to Weeks and Dean's 1977 paper and Sansone and Tewari's 1978 paper, and similar cell design features. Much of the basic understanding of the...
barrier properties of CPC was established during this period, with a large battery of gloves (28) being tested with a wide range of solvents (29).

![Nelson's permeation cell (1981)](image)

**Figure 10 Nelson's permeation cell (1981)**

The advantages of Nelson et al.’s (1981) cell design included ruggedness and chemical resistance. An inlet air stream directed at the test sample removes permeant, and the horizontal sample orientation ensures good contact between test chemical and the test sample. However the cell design has a large dead volume and there is some ambiguity as to the actual exposed area as the O-ring seal describes an area larger than the exposed and collecting areas of the sample. The three bolts holding the cell together limit the cell's application to excised samples of CPC. Sixty-minute runs were used, limiting the application of the permeation data to short tasks. An airflow of 25 Lpm permitted the effective use of a Miran infrared analyser. A protective trap was used between the permeation cell and the analyser. This trap would further increase the system’s dead volume and reduce the ability of the system to resolve changes in permeation rate.

Nelson et al. (1981) advanced the state of the art by attempting modelling of the permeation with a thermodynamic approach, but they accepted the findings of others (Coletta et al., 1978) quoting “such modelling appears to be impracticable at this time”. Five types of permeation curve were characterised in terms of polymer-solvent interactions, but mechanisms to describe the curves were not offered. Two Miran 1A
analysers were used for binary mixtures and synergism of permeation was demonstrated for a pentane-trichloroethylene mixture with polyethylene glove.

Eventually, there were a number of challenges to the ASTM cell, mainly on its mechanical properties, not its performance. Jencen and Hardy (1988) saw the cell as fragile, requiring external support and being "difficult to manipulate". They also circulated the challenge chemical through their stainless steel permeation cell rather than leaving it static or stirred. Lara et al. (1992b) noted that the ASTM cell was expensive, complex and required a well-trained operator. Davis et al. (1986) made a stainless steel version of the ASTM cell to overcome the problems associated with glass.

SECTION 2.7 PERMEATION CELL DESIGN CRITERIA

Only two examples of a rationale for permeation cell design have been found in the literature. The first was a design criteria for a permeation cell by Leinster et al. (1986) for the "British Occupational Hygiene Society Technical Committee Working Party on Protective Clothing" to replace the ASTM cell that was seen as "unnecessarily large" and had a poor seal. They considered the following points important.

- A known exposed area of test material,
- use of chemically inert material like glass, stainless steel or Teflon®,
- keeping pipework short,
- efficient evaporation of permeant, and
- ensuring sufficient chemical to keep test sample covered.

The paper also discussed operational parameters like collecting flow rate, open or closed loop testing, collection media and test temperatures. These criteria resulted in the ISO cell. Ease of use, decontamination and collecting flow patterns were not discussed.
A second set of design criteria in a specification for a gravimetric cell for use in field test was given by Schwope et al. (1988b). They wrote:

“Such a field test should:

1. Provide some indication of "breakthrough time: and "permeation rate" (But, it is not necessary that the specific permeant of a mixture be identified). In other words, the permeation of any chemical, regardless of its toxicity, would be interpreted as breach of the barrier. Also, it is not necessary that the test actually measure breakthrough time or permeation rate in cases where a good correlation exists between the results of other tests and these parameters.

2. Be durable, portable, and self contained and require no external power source (The number of parts should be small)

3. Be simple and easy to learn and perform (minimal calibration should be required.)

4. Be of immediate benefit, requiring minimal development time and cost.

5. At a minimum, be applicable to a wide variety of liquid organic chemicals.”

In some cases it was obvious that a cell had specific features, but the reason for other features was usually not given. As an example, Fricker and Hardy's cell (1992) for testing solids is shown in Figure 12.
The essential element in Fricker and Hardy’s cell design was a plunger to ensure the solid test chemical remains in constant contact with the test sample. This feature could be incorporated into any permeation cell with an open ended cylindrical body (such as Williams' 1979 cell in Figure 6), by the addition of a plunger. Other features like the configuration of the collecting volume were not explained.

A more extensive catalogue of published cell designs with their apparent weaknesses and strengths is presented in Appendix A "Cell Designs", but some of these features of two-compartment cells are given in Table 2.
Table 2 Features of some two-compartment permeation cells

<table>
<thead>
<tr>
<th>Cell described by</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linch (1971)</td>
<td>Simple, ASTM F739-like glass cell with six clamping wingnuts and a horizontal test sample.</td>
</tr>
<tr>
<td>Weeks and Dean (1977)</td>
<td>Another ASTM F739-like cell. Simple, but fragile with a vertical sample and poor sample clamping.</td>
</tr>
<tr>
<td>Sansone and Tewari (1978)</td>
<td>Closed loop glass cell Glass, with a sprung clamp and &quot;O&quot;- ring seals. Low challenge liquid chemical volume (~2 mL). Samples taken with a 2 μL micro-syringe for analysis by GC- FID.</td>
</tr>
<tr>
<td>Berardinelli et al. (1983)</td>
<td>Variant of MAK for open loop measurements. The collection volume of this cell was 20.4 mL</td>
</tr>
<tr>
<td>Williams (1979)</td>
<td>ISO-like cell clamped by 3 bolts with sample horizontal. The cells designed appear to be rugged, with similarities to both the ASTM F739 and ISO cells.</td>
</tr>
<tr>
<td>Williams (1980)</td>
<td>Variant of above with central inlet, free standing and a single central clamp for use with whole garment. Torque screwdriver was used on the clamp.</td>
</tr>
<tr>
<td>Sansone and Tewari (1980)</td>
<td>Stainless steel permeation cell with a wire mesh disk to support the test sample.</td>
</tr>
<tr>
<td>Nelson et al. (1981)</td>
<td>Used with organic solvents at high flows (25 Lpm) to Miran 1A infrared analyser. Large dead volume of the cell and overflow trap.</td>
</tr>
<tr>
<td>Leinster et al. (1986)</td>
<td>ISO cell. The cell is rugged, simple to fabricate from metal and easy to decontaminate. Not free standing and uses multiple bolts. Large dead volume. Designed for use with solvents.</td>
</tr>
<tr>
<td>Stampfer et al. (1984a)</td>
<td>For polychlorinated biphenols. Appears to be made from hydraulic brake fittings. Large collecting volume. For closed loop testing.</td>
</tr>
<tr>
<td>Davis et al. (1986)</td>
<td>Stainless steel ASTM F739 cell to avoid breakage. Expensive, and sample no longer visible during testing.</td>
</tr>
<tr>
<td>Forsberg and Faniadis (1986)</td>
<td>The cell is simple and quick to assemble due to the single clamp. Can be used with intact CPC garments. Large (25 mL) collecting volume. Only suitable for liquids and there is no way to &quot;top up&quot; the cell during use.</td>
</tr>
<tr>
<td>Mellstrom et al. (1989).</td>
<td>Three cells: Stainless steel &quot;FMD&quot; cell and a cover glass sealing and small volume; Teflon &quot;R&quot; cell, also stainless steel and larger; &quot;T&quot; or &quot;Scandcell&quot;. Single central clamp.</td>
</tr>
<tr>
<td>Ehntholt et al. (1990)</td>
<td>Horizontal cell with a solid - silicon rubber collecting medium in the top half, to permit regular replacement and analysis. For low vapour pressure and water insoluble chemicals. Cumbersome and fragile.</td>
</tr>
<tr>
<td>Fricker (PhD thesis, 1992)</td>
<td>ISO-like cell for use with solid chemicals. A plunger ensured the solid chemical was kept in contact with the CPC.</td>
</tr>
</tbody>
</table>

SECTION 2.8 TEST SYSTEMS

There have been a number of test systems described that simultaneously test more than one permeation sample. These have used extensions of automation associated with gas and liquid chromatography systems (Williams, 1979; Moody and Ritter, 1990). Perkins and Ridge (1986a) refer to a 1983 Radian GC system that "performs three tests and a
blank simultaneously" and "saves time". The number of permeation cells that have been tested simultaneously range from two to eight.

### 2.8.1 Multiple Components

Two basic approaches for the measurement of multiple components have been described, one using multiple detectors (Nelson *et al.*, 1981; Berardinelli and Moyer, 1987) and the other using a detector that measures several components simultaneously (Moody and Ritter, 1990; Reed and Cook, 1997). Both Nelson and Berardinelli used multiple Miran IR analysers to simultaneously measure two components. The use of Miran analysers was discounted by Perkins and Ridge (1986a) who concluded (for single analysers) that "*in-series or parallel testing is not recommended with the Miran*" as the purge times were excessive and there were problems with instrument sensitivity. Most multi-component detectors rely on gas chromatography with increasingly sophisticated chromatography software to run the whole experiment, including the sequencing of valves and logging of data. There have also been some developments in stand-alone automated permeation test systems as follows.

### 2.8.2 Automated Systems

Jencen and Hardy (1988) noted that the "*study of glove permeation is amenable to computer control and automation*" and interfaced a personal computer (PC) to a FID on a GC. In 1988, the power of personal computers (PC) was relatively low and the software, though capable of complex tasks, was not graphically orientated. Perkins and Ridge (1986b) used a PC with GC software to sequence valves that switched the collecting flows from a GC to a photoionisation detector. Stull and Pinette (1990a) used an "*automated permeation system*" that used three cells, a blank cell and a reference toluene atmosphere, with flows to a photoionisation detector sequenced by a computer. It is not known whether the system incorporated data acquisition and manipulation capabilities. Several automated systems are mentioned by Henry (1990), including the Radian Corporation's system and a ProTech "*fully automated permeation system*".
No details of either system were given nor their availability, but it appears the Protech system tests four cells and may be used with a gas chromatograph. Perkins reported the use of commercial permeation data from the Radian Corporation (Perkins et al., 1986b). More recently Anna et al. (1988), the sophistication of gas chromatography software from PC based systems has permitted the sequencing of valves and collection and manipulation of sensor data. Manufacturers of gloves possibly have automated systems, but it appears such information is proprietary.

SECTION 2.9 INTERMITTENT EXPOSURE CELL DESIGNS

Few tasks require continuous contact with a chemical for a working day. Tasks tend to involve contact with a chemical and then a period when the chemical either dries or partially dries before contact is again made. The pattern of contact is also variable, with the fingers and palm of gloves usually more exposed than the back or cuff. This may range from single splashes or immersions to cyclic intermittent exposures.

Sansone and Jonas (1981) were probably the first to consider non-continuous exposure. Here, a 100 μL drop of the chemical on a glove sample in their 1980 cell was exposed to the air currents in a fume cupboard. BT was defined as the time when 0.1% (0.1 μg) of the solvent had permeated. The permeation rate was closer to that from liquid than from vapour exposure. They plotted the root of the BT's against the membrane thickness and derived a "critical thickness at and below which the material exhibits no protection against a particular solvent". This work has not been replicated and a theoretical basis for the claim is not obvious.
A Pyrex cell to splash the surface of a test sample with rocket fuels was described by Abernathy and Genova (1991). This cell (Figure 14) splashed the sample for less than five seconds using compressed air. The test chemical then remained in a pool beneath the test sample, creating a saturated atmosphere. Only single exposures appeared to have been used. BTs based on instrument detection limits were reported. The performance of the cell was not compared with that of any other cell.

This splash cell bears a superficial resemblance to the cell developed in this project, but does not have any facility for draining the chemical, drying the test sample nor a provision for ensuring a uniform flow of collecting gas over the collecting side of the test sample. Reversing the airflow through the collecting side of the cell could be expected to improve the collecting flow pattern near the test sample.

Man et al. (1987) simulated intermittent exposure with a partially filled (1-2 mL) ASTM cell (Figure 15), tilting it horizontally to wet the test sample at intervals of 15 or 30 minutes.
After the first splash, the test sample would have been exposed to a nearly saturated solvent vapour but in the workplace, this vapour would dissipate. Man et al. found that with some chemicals, BTs were reduced when compared to data from continuous exposure, but with others, BTs remained constant. With increased total exposure, permeation rates were increased. Wettability of the polymer was found to be a significant factor.

In decontamination studies, Perkins et al. (1987) found "splashing" a butyl chemical suit sample in a similar manner did not allow the sample to dry out properly nor could a good seal with the “exposure cell” be obtained due to the uneven surface of the test material. The exposure cell was described as being made of “two glass hemispheres and gaskets” and appears to be an ASTM F739 type cell.

2.9.1 ASTM F1383 Intermittent exposure cell

Modifications of old cell designs rather than redesign has lead to more complex cells in order to increase their versatility. The modification of the ASTM F739-1996 cell to allow intermittent exposure of CPC exemplifies this and is shown in Figure 16.
This cell is the only intermittent exposure cell that has standing with any standards body (ASTM F1383, 1996). The cell has all the advantages and disadvantages of the standard ASTM cell, but with additional complexity and cost. The additional ports make the intermittent exposure cell larger and more cumbersome than the standard ASTM cell. The cell is manually filled and emptied to simulate intermittent exposure to liquid chemicals in the workplace. However, this process appears slow and filling and emptying might mechanically stress test samples.

A search of the literature did not reveal any experimental intermittent exposure studies with this cell apart from a single set of curves published in the ASTM F1383 standard.

SECTION 2.10 WATER-INSOLUBLE AND LOW VAPOUR PRESSURE CHEMICALS

Water-insoluble and low vapour pressure chemicals present particular problems with traditional two-chambered permeation cells. If a challenge chemical has a low vapour pressure, then it does not readily evaporate and is difficult to collect in collecting gas flow.

Two different methods are examined here. The first uses alternate collection media and the second removes the need for a collection medium.

2.10.1 Alternate Collection Media

For water-soluble chemicals, collection with water or saline has been used (Sansone and Tewari, 1978; Fricker and Hardy, 1994). For test chemicals with low vapour pressure and low water-solubility, non-aqueous collection media have been tried. Solvents may
damage or interact with the CPC sample, making interpretation of the permeation data difficult, though intermittent washing of the sample with a splash of solvent (Pinette et al., 1992f) did give acceptable results. However, it is not known whether the technique might be generally applicable as little is known about any ongoing interaction of the collecting solvent with the CPC sample. There have been some attempts to measure the permeation of such chemicals with alternate methods.

The "slightly modified" version of the ASTM F739-85 cell by Ehntholt et al. (1990) shown in Figure 17 used silicon rubber as the collecting medium, to measure the permeation of pesticides, as "no accepted collecting method for monitoring the permeation of the active ingredients in such formulations exists..."

Figure 17 Ehntholt et al.'s cell with solid collection media (1990)

In reality, the two sides of the cell had completely changed and the sample orientation became horizontal. Only the exposed sample area remained the same as the ASTM F739 cell. A Teflon piston held the silicon rubber collecting medium against the CPC sample. The permeation rate was underestimated as there were problems maintaining contact between the silicon rubber collecting medium and test sample (Pinette et al., 1992f). There was "no apparent immediate solution" to this problem as increasing pressure with the plunger can produce compression of CPC material with a spongy interior. Seams and closures would also limit contact. The use of powdered silicon rubber as a collection medium was not mentioned.
A liquid collecting medium for continuous measurement was considered "not feasible" (Hassler, 1989), but the next year Moody and Ritter (1990) successfully used a liquid flow through their cell and a HPLC detector for pesticide permeation. Flow through light spectroscopy cells have been used in permeation testing of polymer membranes (Liu, 1991).

2.10.2 Fourier Transform Infrared – Attenuated Total Reflectance

Banerjee et al. (1995) investigated the permeation of mustard gas through CPC materials using Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR). The "inside" surface of a CPC sample was placed in contact with an ATR crystal and the evanescent wave (see 7.2.1 on page 1 for an explanation) from total internal reflections inside the crystal was used to measure the concentration of permeant within about two microns of the "inside" surface of the sample. As the permeant did not have to evaporate to be measured, the method was applicable to both water insoluble and low volatility chemicals. The method required that the polymer sample be milled, dissolved in a solvent and then moulded on the ATR crystal. This would not produce an identical sample to that simply excised from a CPC sample and would be unsuitable for pre-formed material like laminates or double dipped gloves.

A similar approach has been taken with human skin, a complex biopolymer, by Bommanann et al. (1990) using FTIR-ATR to examining the thirty cell layers of the stratum corneum, stripped layer by layer from the skin with adhesive tape. Each stripping contained one layer of cells and examination of each layer was analysed. Information was extracted not only about the concentration of water in the layers, but also the changing composition of the skin. A similar FTIR-ATR approach could be applied to CPC to measure permeation and also to investigate the interaction between the permeant and the polymer. However, a method would have to be developed to allow the measurements on excised CPC samples rather than moulded samples to make the method practicable and applicable.

Berardinelli (1995) also suggested the use of FTIR, but with diffuse reflectance. Presumably infrared light would be reflected from the collecting surface of a CPC sample, and the surface spectra of the CPC polymer and emerging permeant would be measured. This could be expected to give a similar result to ATR approaches, but permit the permeant to evaporate. However, the flow over the sample could be critical if low vapour pressure chemicals were tested.
SECTION 2.11 FACTORS AFFECTING PERMEATION MEASUREMENTS AND INTERPRETATION OF PERMEATION DATA

2.11.1 Temperature

Temperature measurement in the testing of CPC is probably the most studied environmental variable, as it is well understood that physical and chemical processes are often strongly temperature dependent. The steady state permeability coefficient “P” is related to the steady state diffusion coefficient “D” and the equilibrium solubility of the solvent in the polymer “S” by the equation

\[ P = DS \]

.................................................................................. Equation 6 Permeability

This may be rewritten (Zellers and Sulewski, 1993) as

\[ P = (D_0 e^{E_p/RT}) (S_0 e^{\Delta H_s/RT}) \]

.................................................................................. Equation 7 Permeability (T)

where \( D_0 \) and \( S_0 \) are constants, \( E_p \) (kcal/mole), is the diffusion activation energy \( \Delta H \) (kcal/mole) is the heat of solution, \( R \) (1.987 x 10^{-3} kcal/mole-K) is the gas constant, \( T \) (K) is the absolute temperature. BT also has an Arrhenius (exponential) dependence on temperature that has some experimental support (Zellers and Sulewski, 1993).

\[ BT = B_0 e^{E_B/RT} \]

........................................ Equation 8 Breakthrough Time (T)

where, \( B_0 \) (min) is a constant and \( E_B \) (kcal/mole) is an activation energy for breakthrough.

The topic of temperature and permeation testing of CPC may be divided into two areas. One area is the actual measurement of temperature and ensuring that an experiment is at that temperature. The other area is the effect of temperature on the permeation process.

**Measurement and regulation of temperature**

The ASTM F739-1996 standard for testing requires that the test temperature be kept within \( \pm 1.0^\circ \text{C} \) and that the test temperature and range of temperatures be reported. Also samples must be conditioned for at least 24 hours at 21\( \pm 5^\circ \text{C} \) before testing. It could be implied that 21°C is the standard test temperature, but this is not stated.

In order to simulate ambient temperatures, skin temperatures and elevated workplace temperatures, different researchers have used different temperatures and methods of
temperature regulation in their permeation experiments. A selection of these is given in Table 3.

### Table 3 Permeation experiment temperatures

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Ambient (°C)</th>
<th>Skin (°C)</th>
<th>Elevated (°C)</th>
<th>Temperature Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nelson et al., 1981</td>
<td>25</td>
<td></td>
<td></td>
<td>Conditioned collecting air at 25°C and 50% RH</td>
</tr>
<tr>
<td>Dillon &amp; Obasuyi, 1985</td>
<td>22.5</td>
<td>45</td>
<td></td>
<td>Constant temperature bath for cell</td>
</tr>
<tr>
<td>Alexy &amp; Buchan, 1987</td>
<td>20</td>
<td>35</td>
<td>50, 65</td>
<td>Oven for cell</td>
</tr>
<tr>
<td>Billing &amp; Bentz, 1988</td>
<td>15, 20, 25</td>
<td>35</td>
<td></td>
<td>No information</td>
</tr>
<tr>
<td>Jencen and Hardy, 1988</td>
<td>25</td>
<td>45</td>
<td></td>
<td>Waterbath 25°±3°C GC oven ±0.01°C control</td>
</tr>
<tr>
<td>Gunderson et al., 1989</td>
<td>25</td>
<td>37</td>
<td></td>
<td>No information</td>
</tr>
<tr>
<td>Stull &amp; Pinette, 1990</td>
<td>25, 27</td>
<td></td>
<td></td>
<td>No information</td>
</tr>
<tr>
<td>Perkins &amp; You, 1992</td>
<td>25</td>
<td>37</td>
<td>50</td>
<td>Waterbath with cell ±1 °C in plastic bag, heating tape for lines and Miran</td>
</tr>
<tr>
<td>Zellers &amp; Sulewski, 1993</td>
<td>25</td>
<td>37</td>
<td>44, 50</td>
<td>Waterbath for cell ±0.5°C, heating mantle for nitrogen, (±1.5°C) and GC syringe</td>
</tr>
<tr>
<td>Anna et al., 1998</td>
<td>25</td>
<td>30, 35</td>
<td>45</td>
<td>Waterbath with modified ASTM cell, ±0.5°C</td>
</tr>
</tbody>
</table>

RH = Relative Humidity

While waterbaths were commonly used, and some attention was given to heating the gas into and from the cell, the use of a GC oven by Jencen and Hardy (1988) appears to have the most potential for easy temperature control. The oven was regulated to ±0.01°C and ramped at rates from 0.1° to 70° a minute from –40°C to several hundred degrees. How well the oven regulated the temperature inside their permeation cell was not stated.

In a recent paper Anna et al. (1998) investigated temperature variations in ASTM F739 cells immersed in a waterbath. Temperature gradients were found between the challenge and collecting side of the cell and vertically within the collecting chamber, and that these gradients increased with test temperature, as expected. A modified ASTM cell (with extended spouts), shown in Figure 18, permitted deep immersion of the cells in a water bath and minimised these gradients to half a degree.
This modification to the ASTM cell may have limited acceptance in testing, as it would make the cell even more fragile.

With the exception of the work by Anna et al. (1988), details of temperature variations inside the permeation cell have been overlooked by other researchers. The option of using a GC oven, which would not have required the cell modification, was not reported.

**Effects of temperature**

Several researchers have reviewed and investigated the effects of temperature on permeation of CPC (Billing Jr and Bentz, 1988; Perkins and You, 1992; Zellers and Sulewski, 1993). Models of the temperature dependence of permeation have all been based on an Arrhenius type relationship. As the temperature increases, the PR increases and the BT decreases.

Hassler (1989) studied the effects of temperature and thickness on BT with pesticide formulations. It was concluded that thick gloves could give greater protection than thin gloves, even when thickness was accounted for, due to the insulating effects of thicker gloves. The thickness of the gloves stopped the heat soaking through.

No published work was found describing the effect of temperature under conditions of intermittent exposure.

**2.11.2 Collecting Flows**

There is no real consensus as to whether flow rates affect permeation indices or whether the flow pattern is important. Collecting flow rates could be expected to affect not only
the removal of permeant from a test sample, but also the response time of the measurement system. The collecting flow patterns may affect the efficiency of removal of permeant from the test sample and the degree of mixing within the collecting volume of the cell.

**Accepted flow rates**

The ASTM F739-1996 standard has a recommended minimum rate of 50 mL min⁻¹ and a recommended maximum rate of 150 mL min⁻¹ for open loop testing. This represents only 0.5 to 1.5 volume changes per minute with the 100 mL collecting chamber in the standard ASTM F739 cell. The recommended lower flow rate was based on minimising saturation of the collecting medium. The high flow rate was required for chemicals with a low solubility in the collection medium or high permeation rates and was also seen by ASTM to "result in better mixing in chamber and consequently more uniform samples".

Mellstrom *et al.* (1989) investigated flow rates as a function of cell volume changes per minute for several types of permeation cell. This data in Figure 19 shows the relationship between flow per unit cell volume and acetone permeation rate through 0.47 mm neoprene. Mellstrom pooled the data and fitted a logarithmic curve, which was said to "fit rather well", to indicate a drop in permeation rate as flow increased. On re-examining Mellstrom's data, a regression coefficient \( r^2 \) of 0.77 was obtained with a logarithmic fit to the pooled data, 0.86 for a power fit and 0.87 for an exponential fit (Figure 19).
An alternative interpretation of Mellstrom's data, using cell flow per unit area of sample is illustrated in Figure 20. This presentation of the data suggests that permeation rates tend to increase rather than decrease with increased flow.

If diffusion is driven by concentration gradients, and poor flow allows the gradient to decrease, then there could be an expectation that up to some limiting flow rate, permeation rates would increase with flow. Mellstrom, did however conclude that both flow rates and flow patterns were "crucial factors", but the apparent relationship
between permeation rate and cell flow could not be generalised. Earlier work involving flow rates by the British Occupational Hygiene Society (Leinster et al., 1986) indicated that flow per unit area was important, but in an inter-laboratory intercomparison, flow changes per collecting volume were still used.

The recent work by Anna et al. (1998) supports this alternate interpretation, as the SSPR was typically underestimated by a factor of two, at the recommended collecting flow rate of 150 mL min\(^{-1}\) (ASTM F739, 1996). Though near ideal mixing was calculated from clearances times of smoke from smoke tubes in the collecting volume of the ASTM F739 cell, there were pockets of stagnation at low flow rates. This was indicated by exhausted smoke when the flow rates were increased.

**Flow rate and detectors**

Some attempts have been made to match the flow rate through the ASTM F739 cell to the detector to give an acceptable system response time. Perkins and Ridge (1986a) tried to increase the flow rate to use the cell with a Miran 1A infrared analyser, and resorted to increasing the size of the holes in the valves on the cell to lessen the pressure drop. Nelson et al.'s cell was designed for an open loop flow of 25 Lpm, to match a Miran 1A analyser.

**Boundary layers**

Boundary layers of permeant next to the test sample have not been directly investigated although the effect of collecting flows at the surface of the sample have been recognised by several researchers. In tests with eleven CPC polymers and four solvents, Stampfer et al. (1984b) found that increasing flow rates in the ASTM F739 cell increased the steady state permeation rate of trichloroethylene with Saranex-laminated Tyvek and plain Saranex. The effect was not reported for any other solvent-polymer pair. The increase in steady state permeation rate with an increased flow rate was attributed to simple dilution of the permeant decreasing the chemical concentration at the surface of the sample and enhancing evaporation of the permeant. Flow rate rather than the flow pattern was considered important. However, it is possible that the increased flow rate increased turbulence in the cell near the sample and decreased the thickness of the boundary layer.

In another paper, Schwope et al. (1988) considered the effect of boundary layers in a field test kit where there was no active flow, only diffusion, to remove the permeant. The BT's were similar for the ASTM permeation cell and their unventilated permeation
cup. However, the permeation rates were almost half for the permeation cup, suggesting that that a significant boundary layer had developed on the inside of the CPC sample, limiting the concentration gradient across the CPC sample. An alternate explanation is that the sample was only partially wet by the chemical.

Recently, Anna et al. (1998) studied flow rates for 44 chemicals through 4 CPC polymers and found that the flow rates recommended by ASTM F739-1996 of 50 mL min\(^{-1}\) in an ASTM cell were inadequate to produce true steady state permeation rates for "a large proportion of solvent/glove pairs". Collecting flow rates rather than disruption of boundary layers were addressed, but regions of stagnation in the ASTM cell and better clearance at higher collecting flow rates were noted. Flow stagnation away from the test sample was not distinguished from stagnation in boundary layers on the test sample.

2.11.3 Sample Thickness

Sample thickness is an important criterion affecting the interpretation of permeation data because greater thickness gives a better barrier property. However, the range of thickness of CPC material is limited by requirements of high dexterity (Williams, 1979; Bensel, 1993; Forsberg and Keith, 1995).

A number of researchers have investigated the effect of thickness on permeation. Adjustments for thickness do permit the performance of the polymers of different CPC samples to be compared, though a simple inverse square of thickness adjustment (Jencen and Hardy, 1989) for Breakthrough Time was shown to be technically erroneous (Schwope et al., 1988) using theoretical models developed by Crank (1975). The permeation of five CPC formulations of two thicknesses, 380 and 635 μm (15 and 25 mil), with five chemicals was measured by Schlatter and Miller (1986). They found that thickness had a greater effect on breakthrough time than permeation rate and also concluded that thicker gloves gave greater protection than expected as they were less likely to have critical defects. The expected inverse relationship of permeation rate to thickness was confirmed by Nelson et al. (1981).

Hassler (1989) found that the thickness of gloves in itself was important in maintaining their barrier properties with hot tasks. Thus if it is assumed that the full thickness of a glove is heated to the solvent temperature during hot solvent degreasing, the actual
barrier properties would be underestimated for short exposures as the inside of the glove is still cool.

**Measurement of thickness**

Little work has been performed to estimate the effect of the method of thickness measurement on the estimate of thickness itself. ASTM F739-1996 requires that the thickness of a CPC samples be "determined to the nearest 0.02 mm" (20 μm), but no detailed technique or specifications as to the number of measurements required is given.

Micrometers are most frequently used and the micrometer's clamping pressure, foot size and the shape of the foot may affect the thickness measurement on spongy polymers. Schwope et al. (1988) reported using an Ono Sokki E.G.-307 digital linear micrometer with a 0.52 cm diameter foot and a 200 g load. Berardinelli and Moyer (1988) measured thickness in 5 places using a gauge with a 4 mm diameter foot. Whether multiple measurements of thickness really result in a better estimate of thickness has not been determined. No research was found that determined the appropriate thickness to ascribe to CPC supported by a strengthening fabric, though preliminary studies by the author did indicate that there was a poor correlation between sample mass and sample thickness for supported samples (Bromwich et al., 1997).

### 2.11.4 Pressure on Sample

The topic of pressure on a CPC sample can be divided into three areas – the effects of pressure on a sample in the workplace, such as gripping a contaminated object; the effects of pressure imbalance on a test sample during permeation testing, causing stretching and thinning of the sample; and the effects of pressure fluctuations caused by high flow rates that cause the sample to vibrate.

**Pressure from tasks**

There appear to be few studies of the effects of pressure due to a task affecting permeation of non-fabric CPC, though Gunderson et al. (1989) examined staining of hands and glove liners with workers using meta-phenylenediamine (MPDA). Staining occurred rapidly through gloves used with contaminated tools at the pressure points. This was explained by the possible development of micro-cracks that permitted partial penetration through the cracks, reducing the effective thickness of the gloves. Pegum and Medhurst (1971) noted dermatitis in orthopaedic surgeons using bone cement in hip replacement operations. The cement was moulded in the palm of one hand and then rammed into the bone cavity with the tips of the right little finger and index finger of the
other hand. These three areas were the areas most affected. Neither study separated the effects of pressure, which would compress the glove, and shear forces, which may produce micro-cracks.

More recently, the effect of flexure of gloves was studied separately by Perkins and Rainey (1997). The greater the amount of flexing of gloves, the smaller the BT, but after an initial period of flexing there was no measurable increase in SSPR. Perkins attributed the changes to the opening of pores within the glove, local thinning of the glove and increased loss of plasticiser (for PVC gloves). Berardinelli et al. (1990) used electron microscopy and found that CPC "may have a fractured surface that is pitted and cratered" that may account for variation they found in permeation. Canning (1997) also used electron microscopy, but to examine and characterise the surfaces of used gloves and found a large variation in new and used gloves and concluded some defects were from manufacture and others from use and chemical exposure.

**Pressure imbalance during testing**

Pressure imbalance across CPC samples could be expected to affect permeation as the sample stretches and thins (Anna et al., 1998). There are no mathematical models to predict the mechanical effects on CPC samples under pressure during testing, though the mathematics of clamped elastic plates is well established (Timoshenko and Woinowsky-Kreiger, 1959). There has been some experimental work where the effect, or lack of effect, of pressure imbalance on permeation have been noted or anticipated.

Williams (1979) found that varying the amount of challenge solvent from 0.5 mL to 25 mL (7 to 327 Pa for liquid chemical density 0.9) did not affect BT, but this work has not been repeated. It suggests that small pressures on small samples may not affect permeation.

Perkins and Ridge (1986a) reported no significant effect of pressure on permeation rate of methylene chloride through Viton, but a possible "small" (20%) effect on BDT. The pressures used were 325 to 2,075 Pa, using an ASTM F739 cell. There was no information as to the degree of bowing of the sample, which would indicate the degree of increase in sample area and thinning of the Viton under pressure.

Schwope et al. (1988) did not report any effect of pressure from a gas flow of 10 Lpm. Jencen and Hardy (1988) noted that "substantial differences in flowpath can distort the
membrane, thus affecting permeation values", but they did not indicate a mechanism. They minimised the pressure differences in their stainless steel cell with its GC-FID detector by keeping lines short and valves large.

More recently Anna et al. (1998) stated that

"The pressure gradient created when using a higher collection stream flow rate should decrease the rate of solvent diffusion through the glove sample"

The reason for this predicted decrease is unclear, as chemical concentration gradients, not pressure gradients are widely thought to affect molecular diffusion. The pressure would derive from the pressure of the collecting gas, not an increased partial pressure of the solvent. Anna also presented a flow-pressure curve for a standard ASTM cell. The data is presented in Figure 21 along with similar data from Perkins and Ridge (1986a).

![Figure 21 Pressure due to collecting flow in a standard ASTM cell](image)

A much larger pressure drop with a standard ASTM cell was recorded by Perkins and Ridge than Anna. Perkins reduced the pressure drop by a factor of 5 to 10 by replacing the 2 mm stopcocks in the ASTM cell with 8 mm stopcocks. Note that not only did the pressure drop change but the rate of pressure increase with flow also decreased markedly due to the reduced flow impedance. The differences between the slope and values in the curves in Figure 21 may be due to either the method of measuring pressure, differences in the stopcock sizes, or other pressure drops imposed on the cells.
In a simple flow-pressure situation, the pressure could be expected to increase with the square of the flow.

The effects of pressure may do more than just thin and enlarge a test sample. The effect of stretching on permeation of organic solvents though polymer membranes was investigated by Sakti (1993) during investigations of PVC and polyethylene (VLDPE, HDPE) geomembranes. Sakti found that significant increases in permeation occurred with 5% elongation. Similar local changes may be expected with CPC during use and in the absence of better data, it may be prudent to limit elongation of a test sample from pressure imbalances to 5% or less.

**Vibration of sample at high flow rates**

Perkins and You (1992) reduced the flow through their system to 4 Lpm to "avoid pressure pulsation effects" with an ASTM cell and MIRAN 1A analyser. Berardinelli and Moyer (1987) used a similar setup and found that the mechanical action of the bellows pump induced "rapid vibration in the test specimen". An aspirator bulb on the cell reduced this effect. In aluminised samples, BT measurements were considerably reduced by cracking which was observed by back-lighting the sample. Lowering the collecting flow rate to 3.5 Lpm did not sufficiently clear the permeant, when compared with BT at the higher flow rate or with a standard ASTM 2" cell. Berardinelli suggested that the effects of vibration "may simulate movements of emergency response workers during a disaster", but no evidence to support this contention was given.

### 2.11.5 Sample Selection, Preparation and Number

The position of a sample from an item of CPC, the way it is treated before testing and the number of samples tested will all affect the interpretation of the permeation data.

**Sample selection**

ASTM F739-1996 requires that "a minimum of three random specimens shall be tested for each material, composite, area (in the case of a heterogeneous design), or other condition." Given the 78 mm diameter sample needed for the ASTM cell, only a limited range of "random" samples can be taken from gloves, particularly from and between the fingers.

In the selection of test samples, Berardinelli and Hall (1985) noted

"An expediency uses a piece or patch of garment from an area which is an acceptable surrogate for the whole. The surrogate time, therefore, should
have a short breakthrough time and large steady state concentration as
compared to the rest of the sites. Additionally, the specimen must be flat
and have a sufficient diameter to fit into a test cell. The glove’s palm and
back met these criteria.”

Berardinelli also found the thinnest sites were between the fingers. The area between the
thumb and forefinger, in particular, tends to be in contact with contaminated surfaces in
gripping tasks and therefore contradicts the choice of palm and back of the glove as an
"acceptable surrogate”.

**Sample preparation**

In attaining a low and stable background prior to a permeation trial, the sample itself
could be viewed as a potential source of contamination. As silicon rubber was used as a
collecting media (Ehntholt *et al.*, 1990), it is reasonable to suppose that polymers would
act as passive samplers, absorbing vapours from the air or emitting vapours from
volatiles left in the material from manufacture.

Davis *et al.* (1986) left the test sample in his test cell for 1½ hours before measurement
to "allow for vaporization of volatile compounds from the glove specimens and, thus, to
establish a steady FID response baseline." Other researchers have used prolonged pre-
test periods to reduce background levels (Williams, 1979).

Active methods of pre-treatment of samples could reduce residual contamination in a
similar manner to CPC decontamination (Perkins, 1991), but these methods have not
been applied to CPC sample preparation.

**Number of samples**

In determining the number of tests to perform using the ASTM F739-1996 protocol, or
to demonstrate cell equivalence, it appears that the choice of three replicates is an
arbitrary choice with a limited statistical basis. It is possible that the cost of testing a
statistically significant number of samples is prohibitive. Perkins (1987b) noted that
"three (tests) is not a large sample size" when commenting on the variability of test
results. Schlatter (1988), in reporting the work of Mickelsen (1986) claimed that seven
replicates were needed to be “statistically significant” in detecting differences in
performance of samples. The degree of variation in permeation was not reported from
Mickelsen *et al*’s unpublished conference paper.
In ranking CPC, small uncertainties in the value of an index will give greater confidence in choice, assuming batch to batch variability is small. Batch variability was investigated by Perkins and Pool (1997) and found it to be significant. Therefore, Perkins considered that "published permeation data ... should be used for guidelines only"

**SECTION 2.12 MODELLING OF CONTINUOUS EXPOSURE**

By modelling the permeation of chemicals through CPC, an insight may be derived into the mechanisms of permeation to make empirical data the basis of prediction of the protective properties of CPC.

Most analytic models used to describe the permeation of chemicals though CPC solve the well-known "Fick's equations" for diffusion. Expansions of these equations by Crank (1975) have been used for simple models of permeation through CPC (Schwope et al., 1988).

As recently as 1987 Alexy and Buchan (1987) stated "mathematical modelling for predicting a garments' protective capability is not yet feasible". In 1988 Goydan et al. (1988a) reviewed methods of modelling permeation of CPC and methods of estimating diffusivity (D) and solubility (S). Cumulative permeation with common rubbery polymers was predicted within an order of magnitude, using an "Equation of State" approach to estimate "S" from molecular weight, vapour pressure and liquid density, and to estimate "D" by a molecular weight corrected method. The authors acknowledged that the assumption of a constant "D" for swollen polymers was likely to be invalid.

Approaches to modelling were also reviewed by Perkins (1990) using permeation studies, "Pat and Weigh" and "Three Dimensional Solubility Parameter" (3DSP) approaches. Perkins found the 3DSP approach offered the greatest potential to predict BT and Permeation Rates (PR) but the complexities of glove formulations limited its general application. For example, Perkins cited the interaction of amine with the small amounts of amine-derived plasticiser in Viton® gloves, which resulted in a degree of permeation not predicted by the properties of Viton. Perkins also called for more research to predict the permeation of mixtures of chemicals, as one component can
change the structure of the polymer, permitting further permeation of the same or another component.

- Most items of CPC are either manufactured from polymers or formed from polymer films, so the developments in polymer science have application in understanding the performance of CPC. Barton, in the CRC "Handbook of Solubility Parameters and Other Cohesion Parameters" (Barton, 1983) graded the increasing sophistication of approaches to the polymer-permeant interactions as
  - **Hildebrand Parameters** for qualitative descriptions giving "good results for a very small number of hydrocarbons" (biochemical and bio-compatible studies);
  - **Hansen Parameters** for an approximate, quantitative measure of interactions, with good results where there are not large chemical interactions (paint formulations, reverse osmosis); and
  - **Sets of Interaction Cohesion Parameters**, including Lewis Acid and Base terms for quantitative assessments (chromatography).

CPC permeation modelling appears to be at the Hansen Parameter stage, with recent advances by Que Hee (1996) to apply chromatography models to CPC. However, Que Hee, assumed that D was constant.

Neogi (1996) recently reviewed diffusion through polymers. Most of his treatment of the subject was for the mass uptake of vapours, not permeation of liquids. One of the most common forms of concentration dependent diffusion was an exponential dependence of diffusion on concentration. Neogi noted that "if the diffusivity is an increasing function of concentration, then a concentration sharpening of the profile takes place and a sharp front is obtained." A hysteresis could then be expected for desorption. An "effective constant diffusivity" was proposed, so long as the diffusion was Fickian.

Most testing and mathematical descriptions of chemical protective clothing assume continuous contact of a challenge chemical with the outside of an item of chemical protective clothing. There is no known work modelling the permeation of CPC except under these conditions of continuous exposure.
2.12.1 Comparison with Empirical Data

In the industrial hygiene literature, there are limited instances where simple CPC permeation models were compared with empirical data. Goydan et al. (1992) investigated 35 chemicals with fluoropolymer coated chemical suits. An "excellent fit to the permeation data was possible using Fick's law with a constant D", was reported, but the details of the fit were not given. Little chemical interaction would be expected with fluoropolymers (Brasure and Ebnesajjad, 1989) and the approach might not be able to be generalised to other CPC polymers.

Zellers et al. (Zellers, 1993; Zellers and Zhang, 1993; Zellers et al., 1996; Zellers et al., 1996) have done fundamental experimental and theoretical work on the application of Hansen’s three-dimensional solubility parameters (3DSP) to predict permeation through CPC, with improvements and simplification of the process. However there has been little recent interest in the application of the 3DSP approaches to predict permeation properties of CPC.

Schwope et al. (1988) performed simple modelling with Lag Times, but the original experimental permeation curves were not shown.

Similarly, from a limited review of the vast polymer literature, only one example was found where a calculated permeation curve (from the diffusion coefficient and solubility), was compared with the original experimental data. In a paper by Uchytil et al. (1996) for acetic acid and water permeating a 35 μm PVA membrane, it was found that a diffusion coefficient that was exponentially dependent on concentration, $D = 10^{10}.e^{4C}$ (i.e., the diffusion coefficient is exponentially proportional to four times the concentration) to permit a good fit to the experimental data. This concentration dependence could also be approximated by a constant diffusion coefficient of $1.6 \times 10^{-9}$ cm$^2$s$^{-1}$ coupled with a delay of 1600 seconds. The mathematical basis for this approach can be found in Crank (1975).

Crank (1975) recognised that in the "diffusion of vapours in high-polymer substances, the concentration dependence is a very marked characteristic function". A number of expressions for diffusion that also varied with concentration, including an exponential dependence, were suggested.
SECTION 2.13 MODELLING OF INTERMITTENT EXPOSURE

No mathematical models of permeation of CPC under conditions of cyclic intermittent exposure, such as described in ASTM F1383-1996, appear to have been published. Crank (1975) discusses sorption and desorption curves and sinusoidally varying concentrations of gases, but this does not directly translate to cyclic intermittent exposure of liquids. It may be possible to construct simple analytic models of cyclic intermittent exposure using Fourier Analysis, but these models may not have analytic solutions if complexities such as concentration dependent diffusion and temperature gradients are included. Thus analytic approaches may not provide useful solutions to emulate real conditions.

SECTION 2.14 SUMMARY OF LITERATURE REVIEW FINDINGS

The evolution of permeation testing has been directed more at determining permeation data than understanding the permeation process and developing standard methods. Large batteries of chemicals and CPC samples feature in a number of studies.

Test methods
The ASTM F739 test method in its 1991, 1985 and 1996 implementations has been the basis of most research in CPC permeation. There was no published research using the newer ASTM F1383-1996 method for intermittent exposure at the time of writing.

Test systems
Most permeation test systems used the ASTM cell with gas chromatography, PID analysers or Miran analysers. With sophisticated software in GC systems and the use of personal computers, there has been a trend to varying degrees of automation of permeation testing. In most multi-cell systems, only a single analyser was used for all the cells. Commercial permeation systems are not commonly used in research.

Cell designs
There was a lack of a comprehensive design criteria for permeation cells for CPC, evidenced by the range of designs and unexplained design features. No single cell could meet all the performance requirements suggested or implied by different researchers.

Intermittent exposure cell designs
The ASTM F1383-1996 intermittent exposure cell can be used to simulate cyclic intermittent exposure but there are no published design criteria for intermittent exposure cells. Other experiments to simulate splashes of solvents have been reported, but there is clearly scope for further research into intermittent exposure cell design.
**Permeation indices**

A limited number of permeation indices have gained some acceptance, but their ability to guide the choice and use of chemical protective clothing in the workplace is limited. There was no real indication of the relative degree of variability between similar permeation indices and further investigations into the dependence of breakthrough type indices to detection limits appear warranted. Intermittent exposure was not well understood and may require special indices to allow similar rankings of CPC under intermittent exposure, to compare continuous and intermittent exposure.

**Water-insoluble and low vapour pressure chemicals**

Use of alternate collection media showed some promise but appeared to have limitations due to reproducibility of the data with a solid collecting media or interactions of liquid collecting media with the test sample. The application of FTIR-ATR for direct and continuous measurement of permeation of water insoluble and low vapour pressure chemicals requires the development of a permeation cell that can test samples from finished garments.

**Factors affecting permeation and the interpretation of permeation data**

- **Temperature**
  The effects of temperature on permeation have been well established but standard test temperatures have not yet been formalised. Recent work has shown that significant temperature gradients may exist in permeation cells when testing with the ASTM cell at elevated temperatures. The temperature at the surfaces of the test samples has not been examined, particularly under conditions of intermittent exposure where the test conditions are cyclically changed.

- **Flow**
  Current research and theory indicates that permeation through a sample depends on the area of the sample rather than the collecting volume. There is little fundamental work on flows inside permeation cells and the required flow regime to remove any boundary layer or the actual pattern of mixing that occurs on the collection side of a cell.

- **Sample thickness**
  The relationship between thickness and permeation appears to be well established, but temperature gradients add an extra dimension, as thickness itself can insulate temperature effects. There has been little work to determine how thickness is best measured, how many measurements of thickness are appropriate or whether the measurement method or technique impacts on the estimate of thickness.
- **Pressure**

Local pressure from tasks appears to increase permeation, but the effect has not been separated from forces that are not normal to the CPC surface that may produce cracks. Pressure imbalances across the sample may affect permeation through stretching, thinning of the sample and re-arrangements of polymer chains. Some work has been done to reduce pressure build-up in cells by modifying cells, but little has been done to design cells that minimise pressure build-up. There is scope to apply the theory of clamped elastic plates to predict the mechanical effects of pressure imbalance on CPC samples. Clearly, there is also a need for a permeation cell design that can cope with a wide range of flows without distorting test samples.

- **Number and choice of samples**

The choice of number of samples used in testing does not appear to be statistically based and the choice of samples from the back or front of the glove, while thinner than the fingertips, may not be the most representative choice to indicate the barrier properties of gloves. This finding is not applicable to CPC manufactured from polymer sheets. Pre-treatment to remove residual contaminants from samples has not been examined.

**Permeation models**

Models of permeation for continuous exposure have had some success, but the modelling of the chemical permeation of CPC still lacks a widely applicable theoretical model to match measured performance of CPC. There are no known models to emulate intermittent exposure of CPC.

**SECTION 2.15 CONCLUSIONS**

There has been a considerable amount of research on the permeation of chemicals through CPC, giving considerable information on BT's and permeation rates of individual chemicals and some mixtures through samples of commercial CPC material. However,

- There is a need for a comprehensive set of design criteria for "ideal" permeation cells for testing CPC under conditions of continuous and intermittent exposure to overcome repeatedly stated deficiencies in standard cell designs.
- The method of validation of permeation cells against the standard ASTM cell has not been adequately investigated.
- Sophisticated methods of permeation testing are possible using computers to control multi-celled permeation rigs and to acquire and analyse data.
• Work with intermittent exposure cells is in its infancy and there are presently no real alternatives to the ASTM intermittent exposure cell.

• The standard methods of measuring the permeation of CPC are not applicable to chemicals that are solids or have low vapour pressures and are water insoluble. Some alternate methods have been suggested, but alternative methods, for example, ATR, have not been applied to finished items of CPC.

• The choice and application of permeation indices still requires attention and there is inadequate information as to the uncertainties in the commonly used permeation indices.

• The effects on permeation of collecting flow rate and flow patterns in permeation cells are not well understood. The effects of temperature on permeation have been extensively studied but the effects of pressure during testing require clarification.

• The measurement of the sample thickness deserves further attention.

• Complex models exist to describe permeation under conditions of continuous exposure, but the potential of simple models has not been exhausted, particularly in the modelling of intermittent exposure.
CHAPTER 3. OBJECTIVES

The following objectives for this work were derived from the conclusions in the literature review.

3.1.1 Objective 1

To develop a permeation cell for continuous exposure, that approached the ideal design and produced data equivalent to the existing ASTM F739 standard cell.

The concept of an “ideal” design is based on an examination of the large number of designs that have been published. Some of the features of this ideal will tend to conflict, like low cost and chemical resistance, as chemical resistant components tend to be more expensive. While some design features will be objective and measurable, like dead volumes, others like availability though non-patented design are decidedly subjective. In producing data equivalent to the ASTM F739 cell, this objective recognises the need to link new data to the pool of existing data that has been largely derived using the ASTM cell. In the Literature Review, it was shown (Anna et al., 1998) that the ASTM cell produced erroneous data with some chemicals at its design flow rates. The “ideal” cell should produce better data in these conditions and there is no need for an "ideal" cell to replicate the shortcomings of the ASTM cell. The ASTM cell is just the benchmark by which other cells are judged under a limited set of conditions. However, the degree to which a near “ideal” cell could be tested would be limited by resources, and each parameter could never be fully explored under every combination of condition.

3.1.2 Objective 2

To characterise operational parameters that would affect the measurement and interpretation of permeation data for conditions of continuous exposure.

3.1.3 Objective 3

To investigate an approach to permeation testing for low vapour pressure, water insoluble chemicals and solids, that circumvents the requirement for the chemical to evaporate or dissolve in a collecting medium.

3.1.4 Objective 4

To advance the approaches to permeation testing under conditions of intermittent exposure and develop a model to simulate permeation patterns.
CHAPTER 4. CONTINUOUS EXPOSURE CELLS

SECTION 4.1 AIM

This chapter covers the design and application of two-chambered permeation cells for permeation testing of CPC under conditions of continuous exposure. It includes the following processes:

- Validation of an existing cell, the Griffith cell, against the standard ASTM F739 permeation cell using the ASTM F739-1996 validation criteria;
- development of permeation cell design criteria for an "ideal" cell; and
- validation and appraisal of a cell constructed to meet these design criteria

SECTION 4.2 INTRODUCTION

There is wide recognition of the standard permeation cell published by the American Society for Testing and Materials (ASTM, 1986; 1996) for chemical permeation testing of Chemical Protective Clothing (CPC) materials used to manufacture garments such as chemical suits and gloves. However, the cell is fragile as it is made of glass. Also, it does not specifically direct the flow of the incoming collecting medium to minimise any boundary layer of permeant that may form on the collection side of the test sample. It was designed for fluids and cannot be used to test solid chemicals. It requires about 100 mL of the challenge chemical. It is also slow and tedious to use. Though the ASTM cell was designed to test CPC materials, it is often used to test samples from finished items. It is large and requires a test sample of 68 mm diameter, thus preventing the taking of samples from small items, such as the fingers of gloves. The use of multiple bolts prevents the testing of intact garments. Despite these difficulties and drawbacks, the ASTM cell is still the benchmark that other cells need to meet. A smaller version does exist (Henry III, 1988b), but it is not in common use.

As discussed in the literature review and Appendix A, published cell designs overcome some of the limitations of the ASTM cell but no single design will be "ideal". Some features will tend to be mutually exclusive, such as the chemical resistance and transparency of glass, which conflicts with requirements for ruggedness, and ease of repair. This is a challenge to cell designers, as no single cell could encompass every feature. A cell that is cheap, robust, easy to use and suitable for use with solids, liquids and gases both for the challenge chemical and the collection medium, and on excised
samples from CPC or on intact garments is the objective for the "ideal" cell for routine testing.

To demonstrate equivalence between an alternative new test cell and the ASTM cell, ASTM F739-1996 requires that the test materials are documented, and the tests are reported in a specified manner. It is implied that if the test results are within the ASTM acceptance limits, the alternate cell can be said to be equivalent to the ASTM cell.

Acceptance data for reference neoprene material is published in ASTM F739-1996 and ASTM Committee F-23 has had much foresight in making this material available for testing cells. When the test materials and the challenge chemicals are identical, the requirement for demonstrating equivalence is that the results, in triplicate, are within the acceptance limits for reproducibility (variation between laboratories) and repeatability (variation within a laboratory) published in the standard. Given that Anna et al. (1998) showed that the ASTM cell underestimated the true SSPR at the maximum recommended flow rate of 150 mL min\(^{-1}\), some caution is warranted in assuming that equivalence of cells using the ASTM F739-1996 protocol is good science. It may be fortuitous that this protocol requires the use of a volatile solvent like acetone which would be expected to rapidly desorb from the inside of a CPC test sample into the collecting gas.

Despite some equivalence of alternate cells to the reference cell being demonstrated (Berardinelli et al., 1983; Mellstrom, 1991b) these cells do not appear to have gained wide acceptance. Patton et al. (1988) attempted to validate the proprietary Radian Microcell against the ASTM cell and found that the 1985 draft of an ASTM “Standard Practice for Determining Equivalency of Optional Chemical Permeation Cells to That of the ASTM Cell” was inadequate to determine equivalency.

Modifications to existing cell size (Perkins and Ridge, 1986a) or performance (Renard et al., 1992); the challenge chemical or permeation detection side of the cell (Renard et al., 1992; Fricker and Hardy, 1994); novel cells designs (Berardinelli et al., 1983; Mellstrom et al., 1989); and special cells for field testing (Stull et al., 1992c) have all been suggested, although usually without discussion of functional design criteria. Little has been published to explicitly demonstrate the equivalence of these various cells to the standard ASTM cell.
There was still scope for the evolution of new permeation cells that showed equivalence of performance to the ASTM permeation cell, but took features from existing cells and added new features that addressed limitations in the ASTM cell design. However, without demonstrated equivalence, data for new cells would be isolated from the existing large pool of test data produced using the ASTM cell.

This chapter describes a new test cell, the “Griffith” cell and the process of development and testing of an improved cell, the "Griffith Mk2" cell. The performance and validation of the cells against the published ASTM cell data (ASTM F739, 1996) is described.

**SECTION 4.3  GRIFFITH CELL**

A test cell for measuring the permeation of CPC was developed in 1992 by the author (Bromwich, 1992). This proved to be a cheap and robust alternative to the ASTM cell and it has been used to demonstrate permeation through gloves in undergraduate occupational hygiene laboratory classes. Several hundred students, many with no technical background, have used the cell with minimal training, to test CPC.

The glass ASTM cell was considered unsuitable for student use because the cell was fragile, required too much chemical (causing disposal problems), the test sample was large and thus slow to prepare with scissors and the cost of multiple cells for student use was too great.

The Griffith cell in Figure 22 was designed to meet basic criteria of ruggedness and ease of use.

![Griffith cell in single cell frame](image)

**Figure 22 Griffith cell in single cell frame**
4.3.1 Design of Griffith Cell

The workings of the Griffith cell are shown in Figure 23.

![Griffith cell in heavy frame](image)

The carrier gas enters the cell in the base at “A” and is directed towards the CPC sample at “B” where it collects any permeant in the collecting ring and then exits the cell at “C”, to a detector. Pneumatic connectors (Festo, Brisbane) allow rapid connection and disconnection of the cell from the 6 mm pneumatic lines used in the test system. The connectors screw into the base with a 1/8” British Standard Pipe (BSP) thread. To ensure the assembly does not leak, the cell is held together by a bolt in a frame pushing down on the lid. The bolt is tightened by hand with a handle welded to the top of the bolt, or by a spanner. A “G” clamp is also satisfactory for this purpose. The shape of the cell base is arbitrary and can be square or round. As the cell has a single external clamping bolt, it is possible to use it in situ on an intact glove or chemical suit without cutting the garment. The flat base makes the cell free standing and easy to assemble.

Cell construction is of brass except for the body, which is made of thick walled stainless steel tubing (#316) with an inside diameter of 20.69 ± 0.14 mm. Its outside diameter of 26 mm determined the diameter of the test sample and the collection area in the cell base. This cell is similar to another cell, the ISO cell (Figure 11) which has a diameter of 25 mm and an area of 491 mm$^2$ (Table 4). The Griffith cell is a more compact design than the ISO cell with the carrier gas input and output 180 degrees opposed and in the same plane as the base. The sample sits parallel to the base with the solvent on top under atmospheric pressure. A short section of thick walled stainless steel tube forms the body of the cell and clamps on top of the sample to hold it in place. This also forms a seal between the sample and solvent. This method of clamping has proved to be very effective as a solvent seal and is much simpler and is quicker than the ISO cell with its bolts that also require four holes to be cut in each sample. The ISO cell does not sit flat and must be held in a clamp. The Griffith cell is able to placed on a bench top and many
can be placed close together, whereas the ISO cell must be clamped in a stand because of the orientation of the carrier gas input and output ports.

4.3.2 Initial Use of the Griffith Cell

The Griffith cell was designed to work with stain tubes (Bromwich, 1992) acting as integrating detectors. This enabled many students to test glove samples at the same time without the high cost of electronic detectors.

![Griffith cell, with stain tube and SKC sampling pump](image)

Air was blown by the pump through the stain tube to avoid the solvent-swollen sample occluding the exit port of the cell. The flow though the stain tube was matched to give the same flow as if the stain tube pump was attached. The total flow through the stain tube would have exceeded the total design flow for the stain tube, but that was not thought to be a significant factor. Both Drager and Kitagawa (cheaper) stain tubes were used, but with different flow rates. The results were considered semi-quantitative and could be used to rank choices.

A similar stain tube technique has also been used by Williams (1979) and also Carrol et al. (1992). ASTM F739-1996 mentions the use of stain tubes as detectors.

SECTION 4.4 THE GLOVETEST SYSTEM

A prototype permeation testing rig was built during a funded project (Bromwich et al., 1997) for which the author was the chief investigator. The design concept was retained for this work, although the rig was rebuilt and the software considerably expanded and improved.
The design evolved to allow sequential measurement of up to 8 cells, sequenced by a commercial Programmable Logic Controller (PLC) so that a single photoionisation detector (PID) could be used. Other researchers have used multiple detectors (Berardinelli et al., 1990), avoiding this complexity, but adding considerably to costs and the need to calibrate multiple detectors. With a cheap personal computer at the heart of the system interrogating a 12 bit 16 channel analogue to digital (A-D) converter board and controlling a 16 channel PLC card, a powerful and flexible test rig was constructed. The PID, flow, temperature and pressure sensors were interfaced with the A-D board.

The test rig is shown schematically in Figure 25. Electrical connections are shown as single lines and gas flows as double lines.

![Figure 25 GloveTest hardware schematic](image)

The main feature of the test rig is a high degree of automation while testing eight cells in sequence in a one-minute cycle, with no intervention once the challenge solvent is placed in each cell. The test rig is also capable of rapid re-configuration through software changes and quick connect fittings between most elements.

Details of the hardware of the test system (the GloveTest rig) and associated elements are provided in Appendix B and details of the GloveTest software are given in Appendix C.
SECTION 4.5  CELL CLAMPING FRAMES

The design of a permeation cell determines the need for a separate clamping arrangement, particularly if the cell has a single, central clamp. Cells bolted together with multiple bolts do not require an external clamp. To seal the cell in teaching laboratories, either a clamp such as used in woodworking, or a custom clamp could have been used. As suitable off-cuts of an 80 mm square extruded aluminium section with 6 mm walls were available, these were readily made into clamps with the addition of a bolt. A handle was welded to the bolt to facilitate use without a spanner. This frame is shown in Figure 22. As each clamp is separate, the rigidity of each clamp was not a major concern, as long as obvious distortion did not occur during use. These simple frames were also adapted for use in special tests (such as determination of the effects of flow patterns and the effects of flow rate on pressure) where inversion of the cell was needed.

4.5.1 GloveTest Frame

The single cell frames were satisfactory for testing single cells. However, with the development of the GloveTest rig for testing eight samples simultaneously, a heavier, steel frame was developed to allow eight cells to be tested at once. Individual clamps created too much bulk.

![Figure 26 Steel clamping frame with Griffith cells](image)

The cells were clamped into the reinforced steel frame on the laboratory bench and then connected to the test rig. The reinforcement was required so that tightening of one cell did not reduce the clamping pressure on another cell. With practice, repeatable tightening was achieved by hand, using a screwdriver handle with a socket wrench.

SECTION 4.6  GRIFFITH CELL VALIDATION EXPERIMENTS

The validation of a permeation cell to ASTM F739-1996 required the development of a system for reproducibly measuring the permeation of acetone through neoprene reference samples, and a method of collecting the permeation data. The advent of cheap personal computers, data acquisition and control cards, and easy-to-use software, has
enabled automation of much of the testing and allows a more rigorous approach. It has also permitted rapid and precise collection and analysis of test data. The developments in cell design need to match those in experiment automation.

4.6.1 Detection Limits
For a given test cell, sample and challenge chemical, the system detection limit depends on the range setting of the PID, the degree of decontamination of the system prior to a test and the nitrogen flow rate. For acetone in nitrogen for normal runs (using the highest range of the PID of 5000, and 500 mL min\(^{-1}\) nitrogen) with multiple cells, this was 0.1 μg cm\(^{-2}\)min\(^{-1}\) with the Griffith cell, determined as two SD of the signal above background. With careful decontamination of the PID, reduced flow rates (100 mL min\(^{-1}\)), and the lowest range setting on the PID (of 50 rather than 5000), the detection limit could be reduced to less than 0.004±0.001 μg cm\(^{-2}\)min\(^{-1}\), if only a single cell was monitored. Thus, the design of the experiments was dictated by the required detection limits.

4.6.2 Temperature of Testing
ASTM F739 does not specify where the temperature of the experiment should be measured. Isothermal conditions for the experiment were generated by ensuring the room was air-conditioned continuously and that the experiment was placed near the room air return, to ensure the most stable conditions. The experiment temperature was the same on the outside of the cells, in the nitrogen flow from the cell to the detector and in the room, to within 1°C. Experiment and room temperature were 21±1°C at all times and relative humidity was usually between 45% and 69%. The sample storage conditions required by ASTM F739-1996 are 21±5°C with a relative humidity of 30 to 80. The test temperature has not yet been standardised by ASTM F739-1996, but the SSPR could be expected to increase with temperature, making comparisons of testing performed at different temperatures difficult.

Anna et al. (1998) recently evaluated the variation of temperature in an ASTM F739 cell and found that shallow immersion could reduce gradients to ±1°C, so long as the temperature was ambient. Complete immersion of a modified ASTM cell could reduce this to variation to ±0.5 °C, even with elevated test temperatures.
4.6.3 Measurement of Temperature, Flow and Solvent Concentration

The temperature transducer (LM335, National Semiconductor, Santa Clara, California. [http://www.national.com/pf/LM/LM335.html]) was calibrated with a NATA³ certified mercury thermometer. The mercury thermometer was placed in a transparent tube in the airflow past the temperature transducer to ensure "immersion" of the thermometer.

A compensated mass flow sensor (AW5000, Honeywell Sensing & Control, Sydney. [http://www.honeywell.com/sensing/prodinfo/massairflow/catalog/71.pdf]) was check calibrated by a bubble tube (Gillian 800268 meter with a D800286 20-to-6000 mL min⁻¹ certified flow sensor, Selby Scientific, Brisbane) and placed before a photoionisation detector or PID (HNU 101, Selby Scientific, Brisbane. [http://www.hnu.com]). Two alternatives were considered to measure the collecting flow from the cells, as shown in Figure 27.

![Diagram of measurement of flow from cells]

Figure 27 Measurement of flow from cells

Note that each cell has a metering valve and poppet valve and the flow through each cell is directed in sequence through its poppet valve to the collecting duct. The main pressure drop in the system is at the metering valve so small differences in the pressure drop downstream from the valve make no difference to the flow. The system from the collecting duct downstream is common to all cells. Option "A" alternates the effluent


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flow between a flow past the PID and a flow through the mass flow sensor. Option "B" passes all the flow through the mass flow sensor and then past the PID.

Option "A" was chosen though it was more complex, as it minimised chemical exposure to the mass flow sensor and minimised the dead volume between the cell and the PID. Both option "A" and "B" gave the same flow through the mass flow sensor. The flow sensor's calibration curve was programmed into the test software to read as mL min\(^{-1}\).

A flow rate of between 50 and 150 mL min\(^{-1}\) for the collecting gas is “recommended” for the ASTM-F739 cell, with adequacy of mixing of the collection media in the cell as the rationale for the lower flow rate. Anna et al (1998) found that 150 mL min\(^{-1}\) inadequate to measure the true SSPR with many solvents. A higher rate of 50 mL min\(^{-1}\) was suggested. Despite this finding, it the upper flow rate of 150 mL min\(^{-1}\) appeared in the August 1999 version of ASTM F739 (ASTM F739, 1999a). No rationale was given for the upper flow rate, so the upper flow rate was taken as guidance, not as a mandatory requirement. Anna et al. (1998) found 150 mL min\(^{-1}\) inadequate “for a large proportion of solvent/glove pairs”. They tested 4 glove materials with 44 solvents. In this experiment, a nitrogen flow rate of at least 2000 mL min\(^{-1}\), or dilution of the effluent flow, was required to match the acetone concentrations from the ASTM cell to the PID detector. The effects of flow on permeation are discussed in Chapter 5, though it was found that the steady state permeation rate for the Griffith cell was essentially unaffected between 400 and 7000 mL min\(^{-1}\). At a flow rate below 400 mL min\(^{-1}\), the PID was off-scale and at 7000 mL min\(^{-1}\) the neoprene sample vibrated so violently that the acetone was sprayed from the filling hole in the cell lid. Flow rates of 2000 mL min\(^{-1}\) for the ASTM cell and 500 mL min\(^{-1}\) for the Griffith cell were chosen.

The fan inside the PID detector head was sealed and overridden and its flow controlled at 50 mL min\(^{-1}\) by a precision metering valve attached to the laboratory vacuum. This flow rate also placed a lower limit on the collection flow through the permeation cells. The PID was calibrated with zero to 11 μL of acetone using a 10 μL micro-syringe (SGE) in 4 litres of nitrogen in a 5 litre Tedlar® sampling bag (SKC). The volume was measured by filling an evacuated bag at a precise flow rate (set around 1 Lpm) for a precise time (±1 ms). Solenoids controlled the flow of nitrogen. The experimental details for the automated Tedlar bag flushing and filling are given in Appendix B.
Liquid test chemical was introduced into the cell with a pipette through the lid, wetting the upper surface of the CPC sample. An adequate seal was formed between both the body and the base of the cell and the CPC sample, without any additional gaskets. The liquid test chemical then began to permeate the CPC sample by diffusion and was removed from the lower surface of the CPC sample cell by a carrier gas.

Decontamination of the cells between runs was done for 15 minutes at 60°C in a vacuum oven made from a circular electric frying pan (Kambrook, Australia) with a lid of 13 mm polycarbonate sheet. The low decontamination temperature was necessitated by the 60°C temperature rating of the O-ring seals in the pneumatic connectors.

4.6.4 The ASTM F739 Standard Cell

Although not needed for the comparison of the Griffith cell to published ASTM cell data, an ASTM F739 cell was constructed (Figure 28) by a local scientific glass company (Labglass, Brisbane) with drawings from ASTM F739-1996. This allowed the shape of an ASTM cell permeation curve to be qualitatively compared with the Griffith cell permeation curves.

![Figure 28 ASTM F739 cell used in trials](image)

Rather than a metal clamp with three bolts to hold the cell, a PVC clamp with six bolts was made to hold the cell together. This had some “give” and proved to be satisfactory. The cell was used without gaskets as it was found to seal well with the neoprene sample material, if carefully tightened. The actual diameter of the wetted sample area of the ASTM cell was 42.92 ±2.96 mm compared with the 51 mm specified in ASTM F739-1996. This size disparity was of some concern, but the main objective of this experiment was to compare the Griffith cell with the published ASTM data, and a miniature 25 mm version of the ASTM cell had been said to be comparable (Henry III, 1988b) to the
standard ASTM cell. The ASTM cell specification (ASTM F739, 1996) had a glass stirrer, but this was not used as adequate turbulent mixing was expected at the flow rate of 2000 mL min\(^{-1}\) used to achieve a similar flow rate per unit sample area to the Griffith cell. Other researchers (Anna et al., 1998) used a version of the ASTM-739 cell that is designed for open loop testing that has a smaller collecting volume and no stirrer that.

Table 4 shows the flow rates through the cells to give the same flow rate per unit sample area.

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Sample Diameter (mm)</th>
<th>Sample Area (cm(^2))</th>
<th>Collection flow for same flow : area ratio (mL min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Griffith</td>
<td>21.7</td>
<td>3.7</td>
<td>500</td>
</tr>
<tr>
<td>Griffith Small</td>
<td>9.5</td>
<td>0.71</td>
<td>96</td>
</tr>
<tr>
<td>ISO</td>
<td>25</td>
<td>4.9</td>
<td>664</td>
</tr>
<tr>
<td>ASTM</td>
<td>44</td>
<td>15.2</td>
<td>2056</td>
</tr>
</tbody>
</table>

The flow rate of 2056 mL min\(^{-1}\) was much greater than the 500 mL min\(^{-1}\) specified in ASTM F739-1986 and well above the 150 mL min\(^{-1}\) in ASTM F739-1996. This collection flow rate was required to match the effluent concentration to the range of the photo-ionisation detector and is supported by the work on flow rates in ASTM F739 cells by Anna et al. (1998). Earlier attempts by the author (Bromwich et al., 1997) had made use of a dilution chamber to mix a 500 mL min\(^{-1}\) flow from the cell with another fixed 1500 mL min\(^{-1}\) of nitrogen, just before the detector.

Dilution chamber "C", with its internal baffle visible in Figure 29, was used as it provided the best mixing and lowest volume. The dilution chamber was removed from the system when a flow transducer with a greater flow range was purchased. A replacement higher capacity flow meter permitted the flow through the cell to be set and monitored directly.
4.6.5 Test Materials

As stated previously, Committee F23 of ASTM has shown much foresight in making available, for testing permeation cells, samples of 400 μm neoprene sheet from the same stock used for their published figures in ASTM F739-1996. This reference material was used in this experiment and is referred to as reference neoprene. Acetone (Ajax Chemicals, analytic reagent grade) was used as the challenge chemical as suggested by ASTM, and for calibrating the PID sensor.

4.6.6 Permeation Experiments

Two experiments were performed to demonstrate the Griffith cell to be equivalent to the ASTM cell. The first experiment determined the SSPR and the second determined the nBT.

In the first experiment, to determine the SSPR, six runs of eight cells were performed with the Griffith cells challenging standard neoprene with acetone. The repeat time between successive measurements on each cell was 54 seconds. Two runs were also made with only the ASTM cell and had a repeat time of 7.2 seconds. A nitrogen flow rate (controlled to ±1%) of 500 mL min\(^{-1}\) through the Griffith cells and 2000 mL min\(^{-1}\) through the ASTM cell was used. Prior to each trial, residual contamination was removed from the cells. The three Griffith cells were baked in a vacuum oven at 60°C and the ASTM cell was baked in a hot air oven at 45°C, as it was too bulky to fit in the vacuum oven.

Approximately 1 mL of acetone was then introduced into each Griffith cell on a computer prompt and a start timer for each cell was triggered in the computer. As the ASTM challenge cell volume was nominally 60 mL, the cell was tilted from its vertical orientation during the first few seconds to wet the entire exposed sample with acetone. Filling of the cell could then proceed in a less hurried manner. Once the cells were loaded and the experiment started, the experiment continued for a predetermined 60 minutes. This time was well in excess of the time to reach steady state conditions and about three times the lag time, as suggested by Crank (1975).

The second experiment, to determine nBT required a more thorough decontamination of the test rig prior to each trial. To measure nBT for the permeation cells, as required by ASTM F739-1996, a permeation rate of 0.1 μg cm\(^{-2}\)min\(^{-1}\) must be measured and a
lower, "zero" permeation rate demonstrated. A detection limit is calculated, based on the noise in this zero signal. This very low level must be achieved before the acetone is added to the neoprene test sample. For a sequence of trials, the levels in the system must be cleared from the steady state permeation rate of 200 $\mu$g cm$^{-2}$min$^{-1}$ to a stable figure near 0.01 $\mu$g cm$^{-2}$min$^{-1}$, a factor of 20,000. This was achieved, but was time consuming. However, with multiple cells switching to the one detector, it was not possible to ensure than the residual levels in the system (mainly in the PID) were below the nBT permeation rate. Thus, to measure the nBT, only one cell could be tested in each trial unless separate detectors were used for each cell.

An hour long flushing with high purity nitrogen of the system, PID and cell with sample in place achieved a stable, low background signal from the PID. During this experiment, it was noted that there was a small but immediate response from the PID on addition of the acetone. Several runs were performed with neoprene samples that had been baked in the vacuum oven at 60°C for 15 minutes to determine whether the sample was the source of immediate response.

To allow the second experiment to continue to steady state conditions and demonstrate equivalence between the two experiments, the PID scale had to be changed from 50 to 5000 and the flow rate increased from 100 to 500 mL min$^{-1}$, once breakthrough was evident.

SECTION 4.7 RESULTS OF VALIDATION EXPERIMENTS

4.7.1 Steady State and Normalised Breakthrough Time Results

A graphical view of the data indicates the closeness of the permeation curves. Rather than present all 48 curves, the results from a trial of eight Griffith cells, plus two trials with the ASTM cell are shown in Figure 30. The time of “Breakthrough” is shown in Figure 31 with permeation evident at 9 minutes with most samples. The Normalised Breakthrough Time permeation rate of 0.1 $\mu$g cm$^{-2}$min$^{-1}$ is reached between 9 and 10 minutes.

The summary data for all trials is presented in Table 6.

In the SSPR trials, there was little variation within trials, between trials or between cells. The ASTM cell lagged slightly from the Griffith cell around breakthrough, but
merged with the Griffith cells before steady state conditions occurred. The SSPR of 201.0±7.48 μg/cm²/min (n=48) is 17.6% less than the ASTM-F739 mean of 245 μg/cm²/min, but well within the acceptance limits (Table 5).

For the normalised breakthrough times, the permeation curves in Figure 31 are on a logarithmic scale to emphasise the noise in the signal before breakthrough is detected and the nature of the diffusion process that predicts an immediate but undetectable breakthrough. The permeation rate “zero” just prior to the addition of the acetone was set to a slightly positive value of 0.003 μg cm⁻² min⁻¹ rather than straddling zero, to allow the data to be shown on a logarithmic scale. This small offset has no significant effect on the determination of either the nBT or the SSPR. The effect of pre-treatment of the test samples is discussed in Chapter 5.
Figure 30. Griffith cell permeation curves for Trial B and two ASTM cell runs
4.7.2 Tabulated Permeation Results

The repeatability of the data with the inter-laboratory published data in ASTM F739-1996 is shown in Table 5. The lack of nBT time experimental data for the ASTM F739
cell is due to the initial permeation rate in the ASTM cells being above the nBT permeation rate of 0.1 μg/cm²/min as shown in Figure 32 on a logarithmic scale.

Figure 32 Detection limit of ASTM cell

The lack of sensitivity in detecting a low background with the ASTM cell can be attributed to insufficient decontamination of the ASTM cell prior to the trial, including an insufficient flushing time. The larger sample area of the ASTM cell would have also contributed to the background noise. Extrapolation of the permeation curve for both ASTM trials would give a nBT of 11.5 minutes. While this data is within the ASTM F739-1996 acceptance limits (Table 6), it has not been included in Table 6 as the figure is estimated, not measured.

Table 5 Inter-laboratory reproducibility of data

<table>
<thead>
<tr>
<th>Index</th>
<th>ASTM F739-1996 acceptance data</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Lower Limit</td>
</tr>
<tr>
<td>SSPR (μg cm⁻² min⁻¹)</td>
<td>245</td>
<td>152</td>
</tr>
<tr>
<td>nBT (minutes)</td>
<td>7.2</td>
<td>4.8</td>
</tr>
</tbody>
</table>

SSPR Steady State Permeation Rate
nBT Normalised Breakthrough Time
X No experimental data for ASTM nBT as detection limit for ASTM cell was > 0.1 μg cm⁻² min⁻¹

All the measurements of SSPR and nBT for the Griffith cells and the Griffith ASTM cell were well within the published ASTM acceptance limits, demonstrating excellent
repeatability of permeation under standard conditions for the Griffith cell. Without
details of the experimental set-ups used to obtain the ASTM F739-1996 data, including
experiment temperature, it is not possible to specifically account for inter-laboratory
differences.

The repeatability of the data within this laboratory is shown in Table 6. The SSPR data
are from the first experiment (n = 48) and the nBT data are from the second experiment
(n = 4). The ASTM reproducibility acceptance limits are ±2.8 (or 1.96 \sqrt{2}) of the
coefficient of variation within the ASTM laboratories.

<table>
<thead>
<tr>
<th>Table 6 Repeatability of data from Griffith cell</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Index</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SSPR ((\mu g , cm^{-2} , min^{-1}))</td>
</tr>
<tr>
<td>nBT (min)</td>
</tr>
</tbody>
</table>

SSPR Steady State Permeation Rate
nBT Normalised Breakthrough Time

The repeatability (precision) of the SSPR data is over ten times better than the required
acceptance limits as defined by ASTM. The repeatability of the nBT data is over seven
times better than required. The lower repeatability of the nBT data compared with the
SSPR data relates in part to the averaging of data in the calculation of the SSPR and the
lower number of trials (4 vs 48) conducted for the nBT data. The variability of a number
of permeation indices, including the nBT, is discussed in Chapter 6.

SECTION 4.8 DISCUSSION OF VALIDATION EXPERIMENTS

4.8.1 ASTM F739 Cell Validation Criteria
ASTM F739-1996 has tabulated performance criteria for the ASTM cell based on inter-
laboratory trials involving six laboratories using three polymers challenged with
acetone. (Thirty laboratories would have been statistically desirable, or a more
conservative application of Student’s “t” statistic may have been appropriate to estimate
acceptance limits.) For neoprene, three replicates were used and it appears neoprene was
chosen for validating cells as it gave the most reliable data. Twelve measurements, from
four of the laboratories, appear to have been pooled to produce the acceptance statistics
with a 95% confidence interval.
On this basis, the reproducibility of the ASTM data and repeatability of the data for the two experiments were all well within the acceptance limits recommended by ASTM. The Griffith cell can be said to be equivalent to the ASTM cell within the ASTM F739 (1996) criteria.

### 4.8.2 Steady State Permeation Rates

The coefficient of variation for the 48 Griffith cell SSPR estimates was less than a third of that for the laboratories in the ASTM trials. The reason for this higher degree of reproducibility is not known as limited details were given for the ASTM inter-laboratory trials. Figure 33 shows the permeation curves from Figure 31 on an expanded scale for the period 30 to 60 minutes. The degree of correlation of the permeation curves is more obvious in this figure as there is more variation between cell types than between cells. The greater number (165 vs 16) of measurements were made on the ASTM cells in this period as only one cell was monitored. A slight downward trend after 40 minutes is evident in all the curves.

![Figure 33 Validation Experiment Steady State Permeation](image)

This downward trend might be attributed to swelling of the polymer by the acetone rather than drying of the test sample, since separate tests with various depths of solvent (3 to 15 mm) in the Griffith cell showed no trend (see Chapter 5).
ASTM F739-1996 suggests a flow rate of 50 to 150 mL min$^{-1}$ for the ASTM cell. These flow rates were shown to be low by Anna et al. (1998) supporting the higher (2000 mL min$^{-1}$) flow rates used for the ASTM cell in these trials.

### 4.8.3 Normalised Breakthrough Time

The nBT estimates for the four runs in the second experiment showed the degree of variation to be well within the ASTM acceptance limits, as shown in Table 6.

The use of nBT's in inter-laboratory comparisons do allow measurements at different laboratories to be compared, but limit the development of testing technology. As the nBT is set at an arbitrary, low level, multiple cell test systems with one (expensive) shared detector have to be able to achieve low backgrounds between sequential measurements, inhibiting the testing of a statistically sound number of samples. In these experiments, only one sample could be tested in each trial to determine nBT but eight samples could be tested in each trial for SSPR. The required degree of decontamination of the system between trials was much greater for the nBT determinations. The use of LT would have avoided these problems and made multi-cell testing easier.

### 4.8.4 Lag Time

Other indices exist that permit a ranking of CPC by a breakthrough time. The most popular one is the Lag Time, which is determined from the intercept of the integral of a permeation curve with the time axis. It has the advantage in that it is largely independent of the analytic detection limit. This factor permits multiple cells to be tested at once with some carry-over between cells and a sufficient number of measurements to be performed to give statistical validity to test results.

If the diffusion of the chemical through the CPC can be described by Fick’s laws with a constant diffusion coefficient (D) and thickness ($l$), then the Lag Time can also be directly used to determine the value of D of for the challenge chemical in the polymer. This in turn allows the calculation of the solubility (S) of the solvent in the polymer from the SSPR. The use of Lag Time to determine the diffusion coefficient assumes that D, S and $l$ (no swelling) are constant and do not change with the solvent concentration or time. The value of D must not only be constant under steady state conditions, but also under the initial transitory conditions, or the permeation curve will be shifted. It will be delayed if D is lower under transitory conditions (Uchytil et al., 1996). The fundamental
parameters D and S are then available to predict permeation rates under other conditions (Chapter 6) or more easily the SSPR.

4.8.5 Using Indices to Select CPC

In determining the number of tests to perform using the ASTM F739-1996 protocol, or to demonstrate equivalence, it appears that the choice of three replicates is an arbitrary choice with limited statistical basis. It is possible that closer to seven or eight replicates may be required to demonstrate real differences between sets of measurements on given samples, but the cost of testing a statistically significant number of samples is prohibitive. Schlatter (1988) in reporting the work of Mickelsen (1986) indicated that seven replicates were needed to be “statistically significant” in detecting differences in performance of samples. Such figures are important when designing test systems, as very different approaches would be taken for 3, 8 or even 50 samples.

Two scenarios are presented with best case and worst case selections of CPC. For the worst case, trials were performed in which Ansell single and double dipped PVC gloves were challenged with toluene (Bromwich et al., 1997) to calculate the number of measurements (Table 7) needed to discriminate between the gloves (power 80%, p< 0.05). Although PVC gloves are very popular (Canning, 1997) this data probably represents a worst case as they perform poorly with many common solvents. Calculations for BT, SSPR and LT are given in Table 7.

Table 7 Tests to discriminate Ansell single dipped and double dipped PVC gloves

<table>
<thead>
<tr>
<th>Number of tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSPR</td>
</tr>
<tr>
<td>BT</td>
</tr>
<tr>
<td>LT</td>
</tr>
</tbody>
</table>

Data from the Griffith cell validation experiments with acetone challenging reference neoprene offers a "best case" scenario as the reference neoprene material supplied by ASTM Committee F23 was selected to minimise variations from the test material when comparing cells. The data was also obtained after several more years experience of testing CPC. Table 8 shows that these more precise measurements from challenging the reference neoprene with acetone gave a similar poor ranking for the use of BT. The comparison set of data was generated by varying the means of SSPR, BT and LT by between 5 to 30 %. This gave a second, artificial sets of data (the "artificial set") with different means, but the same variance.
Table 8 Number of tests to discriminate reference neoprene samples using different permeation indices

<table>
<thead>
<tr>
<th>Difference in values of the mean</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSPR</td>
<td>15</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>BT</td>
<td>97</td>
<td>25</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>LT</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

In the scenarios in Table 7 and Table 8, the sensitivity of LT estimates was much greater than BT estimates as fewer tests were required. The number of BT tests required rises rapidly as the true difference between the reference neoprene set and the "artificial set" was reduced from 30% to 5%. In the worst case, PVC glove scenario, only SSPR could be used with three tests to rank the gloves. In the best case scenario, three tests could be used to rationally select CPC between the neoprene data and the "artificial set" when the true BTs varied by a large 30%. However, with the best case scenario and three tests, LT and SSPR could both be estimated with a much greater sensitivity.

The wide ASTM F739-1996 acceptance limits (reproducibility CV 26%) for the nBT indicates that nBT may be a poor index of cell performance (and perhaps not a reliable figure on which to base the selection of CPC). This is also indicated by the expected much greater variability in reproducibility between laboratories than repeatability within a laboratory. The SSPR appears to be a more robust index (CV 22%) as the index has greater reproducibility and a similar repeatability. The data from these experiments indicates the SSPR variability has the most potential for improvement as it had the least scatter. The choice of appropriate performance indices for comparison should eventually lead to more precise numbers being published by manufacturers to assist the CPC user to make the most appropriate choice of CPC.

4.8.6 Griffith Small Cell
A miniature variant of the Griffith cell design was developed to permit sampling from any part of a glove, including those parts with pronounced curvature between the fingers, to use less test chemical and give comparable results to the Griffith cell (Bromwich et al., 1997). This was called the Griffith Small cell.
Chapter 4. Continuous Exposure Cells

This cell has a diameter of 9.5 mm and an effective exposure area of 71 mm². It uses the same clamping system as the Griffith cell.

A factor limiting the utility of any cell is the match between the cell and the response of the chemical detector. To demonstrate equivalence between the new cells and the ASTM F739 cell, measurement of a nBT permeation rate of 0.1 µg cm⁻² min⁻¹ is required. Initial measurements with the Griffith Small cell indicated a detection limit near this permeation rate, making reliable measurements of the nBT permeation rate difficult. Testing was performed with the larger Griffith cell that permitted more sensitive measurements. Eventually, large reductions were achieved in the detection limit through improved decontamination procedures that would have permitted the use of the Griffith Small cell. However, it was decided to use the available resources to develop a better cell, the Griffith Mk2 cell, rather than test the Griffith Small cell.

Details of the dimensions of the Griffith cells are given in Appendix B.

SECTION 4.9 DESIGN CRITERIA FOR PERMEATION CELLS FOR CPC

A two-chambered cell for permeation testing of CPC should:

1. **Test any portion of CPC, intact or excised, including seams.**
   
   To test the performance of a garment, particularly after use, the sample size should be small enough to allow sampling from fingers of gloves. The sealing properties of the test cell should be such that uneven samples incorporating seams can be tested. With a CPC garment, such as a chemical suit, before and after use testing may be needed on the same item, therefore the possibility of *in situ* testing without bolt holes or excision is desirable.

2. **Use with solid, liquid or gas test chemical**
   
   Workplace chemicals are in many physical forms and test cells should be able to handle solids, liquid or gases, so that the chemicals that need testing, not the
chemicals that are easy to test, are evaluated. The testing of solids could be expected to require the pressing of the solid into a pellet and this is most easily achieved in a cylindrical form.

3. **Use with solid, liquid or gas collection medium**

Most test cells use liquids or solids to convey the permeant to a detector. For chemicals with a low vapour pressure or poor solubility in a collection medium that does not affect the test sample, a solid such as silicon rubber has been shown to be a useful alternative (Ehntholt *et al.*, 1990). This approach does restrict the measurement to intermittent sampling, but an alternative is to closely couple a detector to the test sample.

4. **Small dead volume to ensure fast response**

A small dead volume would be expected to permit the collecting medium to be better mixed than a larger collecting volume, and the flushing of this volume fast enough to allow true changes in the rate of permeation to be detected quickly. However, a large collection volume does offer the advantage of possibly containing the contents of a test cell on the mechanical failure of a test sample. The same advantage may be obtained with a trap in the line to the detector, so that the collecting volume may be designed to optimise flow patterns.

A large collecting volume also permits room for the sample to swell, but swelling indicates strong chemical-CPC interactions and a likely poor choice of CPC. With a small positive pressure in the collecting volume, the swelling is more likely to be towards the challenge chemical.

5. **Capable of being used from low flows (50 mL min\(^{-1}\)) to high flows (10 Lpm) of carrier gas without significant pressure on sample.**

By altering the flow rate of the collection medium through the cell, the concentration in the carrier can be varied to match the detector, or even varied continuously to present the detector with a narrow range of concentrations. While not a critical design criterion as the flow can be diluted after leaving the test cell, a cell that is capable of a wide range of collecting flow rates simplifies its use with a range of detectors. It could be expected that this would be more applicable to carrier gases than carrier liquids. Low flow rates are useful to produce maximum sensitivity for instruments like gas chromatographs. Flows of 10 Lpm were used by Perkins and Ridge (1986a) and Schwope *et al.* (1988) both used 10 Lpm with the ASTM-F739 cell.
A high flow rate can stretch the test sample by producing a pressure build-up in the cell. A stretching of 5% both increases the sample area and thins the sample to decrease BT by 10% and increase SSPR by 10%. This level of stretching occurs with a bowing of 1 mm over a 10 mm radius for the Griffith type cell and is taken as the acceptable maximum.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Diameter (mm)</th>
<th>Distension (mm)</th>
<th>Stretch (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Griffith</td>
<td>20</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>ASTM</td>
<td>50</td>
<td>1.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The pressure drop in a system downstream of the test sample, including the permeation cell(s), plumbing and detector may be significant. The ASTM-F739 cell stopcocks was bored out by Perkins and Ridge (1986a) to reduce the pressure drop due to the cell. Keeping the downstream plumbing short and of the maximum practicable bore is necessary to complement good permeation cell design. Some of the cells pictured in the catalogue of cells in Appendix A have small-bore plumbing for the collecting gas flow.

6. **Flow pattern of collection medium to remove boundary layer from the sample**

This criterion is mentioned by a number of researchers, but little has been done to ensure a clean flow regime. Ideally, the flow pattern is such that the flow is directed at the test sample and moves along the surface, scrubbing the surface for permeating chemical. For a well-defined pattern, the flow could start at the centre of the sample and move to the edges, or start at the edge of the sample and move to the centre. Just directing the flow in the direction of the test sample may leave areas where the clearance of permeating chemical is performed less efficiently.

Though the open loop version of the ASTM F739 cell does direct the collecting flow towards the test sample, the increase in permeation rate with flow measured by Anna *et al.* (1988) could indicate that the flow pattern at the surface of the sample was inadequate to remove permeant next to sample.

7. **Easy to decontaminate**

A cell should be easy to decontaminate after each trial. Complex cells with dead spaces and narrow channels are more difficult to clean. This criterion particularly applies to sticky test chemicals and solids.
8. **Quick to assemble and use**
   It would be reasonable to be able to assemble a cell in ten seconds. This precludes the use of multiple bolts and cells that need the sequential tightening of bolts.

9. **Resistant against solvents, acids, alkalis**
   A test cell should be resistant against the same range of chemicals that are used in the workplace. No one material is resistant to all chemicals, but the requirement for ruggedness makes the use of glass as poor choice, though glass cells should be cheap. (The author could not afford the commercial ASTM F739 cells available in the US nor the delays for replacements that would accompany any breakage.)

   As the side of the cell containing the challenge chemical is likely to be more exposed than the collecting volume, it may be possible to construct this part of the cell with acid resistant material like Teflon or quartz. The latter would also make the sample visible.

10. **Little training in use to get reproducible results**
    Test cells should be easy to use, as much of the testing is routine and would use less skilled labour.

11. **Rugged – undamaged by a 1 m drop test onto a hard floor.**
    This should apply to most pieces of occupational hygiene equipment and is essential for field use.

12. **Replaceable components are “off the shelf”**
    For widespread use of a device, ease of repair in the workplace is essential.

13. **Cheap and easy to fabricate**
    If test cells are too complex then their use becomes restricted to research laboratories in the country of origin. The fabrication tolerances should be designed so that precision equipment is not needed for manufacture.

14. **In the public domain (no copyright or royalty)**
    Some test cells are patented and this restricts their wider use.

15. **Can be used in field**
    Field use is desirable, particularly with emergency services.

16. **Capable of being used for intermittent exposure testing**
    Intermittent exposure of CPC to chemicals is moving to mainstream testing as a way of simulating actual workplace exposures of chemicals.
17. Adequate sample size to prevent edge effects

Permeation through part of the clamped area increases the effective exposed area for a very small permeation cell. Simple calculations are sufficient to determine whether corrections are necessary for typical CPC thicknesses.

SECTION 4.10 THE GRIFFITH MK2 CELL

Having validated the basic design of the Griffith cell, an improved version was designed, fulfilling as many of the ideal design criteria as possible. This new version is called the Griffith Mk2 cell. Other criteria could be achieved at a greater cost of materials. For example, construction from stainless steel, quartz or ceramic rather than brass would give corrosive resistance to a wider range of chemicals. (PTFE was considered but rejected as too expensive and easily damaged as it is soft. It would also tend to absorb some solvents, though it was used for the valve in the Griffith Mk2 Intermittent exposure cell in Chapter 8 for its self-lubricating properties. Sintered ceramics would offer most of the advantages except cost and lack of transparency. Use of a glass or quartz body cut from a glass tube in Figure 35 is a possibility that has not been investigated.)

4.10.1 Details of Griffith Mk2 Cell

Like the Griffith cell, the Griffith Mk2 cell is made of brass and is held together by a frame and a single bolt. However, the detail of the cell is somewhat different, as a novel symmetrical radial flow of the collecting fluid has been incorporated in the cell base, which also splits into two pieces for easy decontamination. A nitrile O-ring seals the two parts of the cell base of the standard cell. A more expensive polymer was not required as the O-ring was only exposed to solvent vapours, not the liquid and the system of vacuum over baking removed any contamination. This was verified by the very low pre-trial background solvent concentrations measured in the cell. In practice it was found unnecessary to replace the O-ring frequently. The cell is aligned by means of a stainless steel pin in the base and a ball bearing in the lid.
The chemical (liquid or gas) is introduced to the cell through "C" or "D" which may then be plugged to eliminate evaporation, or connected to a reservoir for gases. Carrier gas (e.g. nitrogen) or liquid (e.g. water) flows into the cell at "A" and is pushed through an annular slot to intercept the test sample and then flow towards the middle of the sample to exit at "B" to be carried to the detector. Pressure on the sample was measured and found to be negligible (~2Pa) at flow rates to 10 Lpm, the highest flow rate that could be metered. Not shown is a small spring-loaded plunger that fits in the top of the cell to permit the testing of solid chemicals.

The location of the annular slit against the cell wall and sheltered by the 2-mm depth of the collecting volume would eliminate the possibility of the slit itself being blocked by a swelling sample. Though the collecting volume was not seen to be blocked when the sample swelled, additional tests with highly swollen samples and direct observation of the sample during the trials would be expected to confirm that the sample did not block the sample volume. The blockage of the sample volume would be expected to be accompanied by a sudden drop in the permeation rate as the collecting area would suddenly be reduced. Any gap would permit the clearance of permeant.

More precise machining of the components of this new cell on a newer lathe than that used for the Griffith cell made each cell almost identical. This was assisted by the design that made the critical dimensions on the cell base easy to machine. The machining of the lid was more complex, but not critical. Overall, it should be possible to replicate this cell on a simple workshop lathe at low cost.

4.10.2 Heavy Frame
The cell clamping arrangement was reviewed with the revision of the GloveTest rig (Appendix B) and development of the new cells. A much heavier frame using bright steel was constructed to hold four cells. A bolted rather than a welded construction of
the frame was used to minimise distortion. For a frame for one cell, this detail would not be critical. This four-cell clamping frame is shown in Figure 36.

![Figure 36 Heavy Frame showing cell and certified torque wrench](image)

A certified 25 inch–pound (2.83 Nm) torque wrench was sourced and this ensured repeatable tightening of the cells. The "M8" bolts (ISO 8 mm coarse thread, 1.25 mm pitch) had a calculated clamping force of 1.8±0.4 kN at a torque of 2.83 Nm, assuming light lubrication and no surface finish (FJ Sweetman & Co, 1996).

**Application of the Heavy Frame for use with intact CPC**

This heavy frame could be used in a variety of configurations Figure 37,
Here, two bolts have been removed and the end support pillar moved to permit the testing of an intact item of CPC.

The ball bearing on the lid of the cell locates with the frame bolt (which has a spherical depression). The bottom of the cell locates on a peg in the frame. This arrangement ensures alignment of the body and base of the cell when used with intact CPC samples.

4.10.3 Validation of Griffith Mk2 Cell against Griffith Cell and ASTM Cell

The cell was validated against the tight spread of data produced with the Griffith cell and found to be the same, thus demonstrating equivalence with the Griffith cell and the ASTM cell.

Three trials (D, E and F) were performed to establish the nBT validation data for the Griffith Mk2 cell. These are shown in Figure 38, pooled with Griffith cell nBT data that were derived for the earlier validation of the Griffith cell against the ASTM acceptance data. The erratic permeation curves below $0.1\ \mu g\ \text{cm}^{-2}\text{min}^{-1}$ were due to a degraded O-ring in the photoionisation detector that trapped contamination between trials, but did not affect the nBT values. Further details are provided in Appendix E.

The nBT and SSPR curves for eight trails of Griffith and Griffith Mk2 cells for acetone vs reference neoprene are shown in Figure 38 and Figure 39, respectively. The measurements were performed in two trials, each with eight cells, alternating between the two cell types.
Figure 38 Normalised Breakthrough Times - Griffith Mk2 cell and Griffith cell
Figure 39 Steady State Permeation Rate for Griffith and Griffith Mk2 cells

- Griffith Mk2 cell (8 trials)
- Griffith cell (8 trials)

Permeation Rate (µg cm² min⁻¹)

Time (min)

ASTM F739 SSPR acceptance limits
Griffith Cell acceptance limits (z statistic)

227.0
203.9

ASTM mean 245
152
Visually, there appears to be no difference between the Griffith cell and Griffith Mk2 cells and both cells are equivalent to the ASTM F739 cell, as demonstrated in the following tables.

**Table 10 Reproducibility (inter-laboratory precision) of Griffith Mk2 cell data to the ASTM F739 and Griffith cells**

<table>
<thead>
<tr>
<th>Index</th>
<th>ASTM F739-1996 acceptance data</th>
<th>Experimental Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Lower Limit</td>
</tr>
<tr>
<td>SSPR (μg cm$^{-2}$min$^{-1}$)</td>
<td>245</td>
<td>152</td>
</tr>
<tr>
<td>nBT (min)</td>
<td>7.2</td>
<td>4.8</td>
</tr>
</tbody>
</table>

SSPR Steady State Permeation Rate  
nBT Normalised Breakthrough Time

The confidence limits for the SSPR and nBT data for the Griffith Mk2 cell are within those for both the ASTM F739 cell and Griffith cell.

**Table 11 Repeatability (intra-laboratory precision) of the Griffith Mk2 cell data**

<table>
<thead>
<tr>
<th>Index</th>
<th>ASTM F739-1996 acceptance data</th>
<th>Experimental Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV</td>
<td>2.8CV</td>
</tr>
<tr>
<td>SSPR (μg cm$^{-2}$min$^{-1}$)</td>
<td>22</td>
<td>62</td>
</tr>
<tr>
<td>(n=8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nBT (min)</td>
<td>12</td>
<td>34</td>
</tr>
<tr>
<td>(n=4)*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SSPR Steady State Permeation Rate  
nBT Normalised Breakthrough Time  
* Griffith cell nBT data were taken from original Griffith cell validation data

The level of repeatability (precision) of SSPR data for the Griffith Mk2 cell is better than that of the Griffith cell and much better than that for the ASTM F739 acceptance data. Only three nBT data points were determined for the Griffith Mk2 cell. This data were similar to the ASTM F739 nBT data but not as good as for the Griffith cell data.

Therefore it can be said that both the Griffith cell and the Griffith Mk2 cell are equivalent to the ASTM F739 cell, and with the exception of repeatability of the Griffith Mk2 nBT data, the Griffith cell and Griffith Mk2 cells are equivalent. Further details of the validation of the Griffith Mk2 cell are given in Appendix E, as they are similar to the Griffith cell validation details.
4.10.4 Cell Size

The size of a sample could be an important consideration in the size of permeation cells, as the clamped area could affect the permeation close to the edge. Crank (1975) discussed the influence of edge effects on membrane permeation. Near the edges of a membrane, diffusion through the membrane spreads into the clamped region. Crank (1975) found that when the exposed diameter was five times the thickness, edge effects could be ignored.

For CPC samples 400 \(\mu\)m thick, the exposed diameter would have to be at least 2 mm to ignore the diameter. The smallest cells (e.g. the Griffith Small cell) used an exposed diameter of 10 mm, so the effect can be ignored. For earlier experiments with PVC gloves using Differential Scanning Calorimeter (DSC) (Bromwich et al., 1997), 3 mm diameter samples were taken. If permeation cells of this very small diameter were considered, then the edge effect could be significant. Sample sizes of the order of 1 cm may be the smallest practicable size to ensure sufficient permeant to enable measurement of a nBT at 0.1 \(\mu\)g/cm\(^2\)/min, but enable relatively flat samples from fingertips and webs of gloves.

4.10.5 Griffith Mk2 Cell and Design Criteria

The design criteria for an "ideal" cell were presented in Section 4.9. The match of the Griffith Mk2 cell to these criteria is discussed.

1. **Test any portion of CPC, intact or excised, including seams.**

   The Griffith Mk2 cell is able to test any region of CPC that is reasonably flat for a 25 mm diameter area. It can be used with excised samples as can the ASTM cell. It can also be used with intact samples by removal of (or machining a bevel on) the locating rim on the cell base. The frame alone ensures the accurate alignment of the top and bottom sections of the cell so that the exposed area and collecting area of the sample precisely coincide. The metal to polymer seal between the cell body and the test sample appeared to work well, and there was no evidence of failure of the seal by early breakthrough.

   No testing has been performed on seams, but it is possible that the seals on the cell would have to be supplemented with an O-ring to account for the uneven thickness, though whole garments have been tested, including gloves (Williams, 1981; Perkins and Pool, 1997). The testing of whole garments overcomes the problem of testing
highly curved regions on gloves between the fingers and the fingertips and to a lesser extent, the fingers themselves.

2. **Use with solid, liquid or gas test chemical**
   The cell testing was only performed with liquids, though the cell lid is sealed to the cell body with an O-ring making it gas tight. The pneumatic connectors in the lid permit the flow of a gaseous challenge chemical, and a small spring-loaded plunger was made to allow the testing of solids in a similar manner to Fricker (1992). However, as solids tend to have a low vapour pressure and may be insoluble in water, a different approach was taken to the measurement of the permeation of solids with FTIR-ATR in Chapter 7.

3. **Use with solid, liquid or gas collection medium**
   The cell was designed to be used with a gas as a collecting fluid, but dye tests with water in Chapter 5 demonstrated that a liquid collection medium is practicable with the cell. Tests to determine the distension of the sample with water flow were not performed and this aspect plus the disruption of boundary layers by a liquid flow remain to be investigated. A solid collecting medium, such as silicon rubber appears not to be practicable with this cell while maintaining a simple and cheap design.

4. **Small dead volume to ensure fast response**
   The cell has a very small dead volume, and the dead volume could be made arbitrarily small by making the upper part of the cell base taller or shortening the collecting ring. The limiting dead volume is then the plumbing downstream of the cell.

5. **Capable of being used from low flows (50 mL min\(^{-1}\)) to high flows (10 L min\(^{-1}\)) of carrier gas without significant pressure on sample.**
   Tests in Chapter 5 showed that the cell can be used over a wide range of flows and give the same permeation rate with acetone. It was also shown that the pressure build-up inside the cell due to the cell design is essentially zero (2 Pa, at most, at the...
sample on the collecting side). There were no oscillations or distension of the test sample at any flow rate, unlike the Griffith cell.

6. **Flow pattern of collection medium to remove boundary layer from the sample**

   Tests of collecting flow pattern in Chapter 5 revealed a near ideal flow pattern with a radially inward, symmetric flow. Though this does not in itself prove removal of the boundary layer, any residual boundary layer would have to be so thin as to be insignificant as the flow velocity at the surface was high and there were no discernible stagnant areas for a significant boundary layer to develop.

7. **Easy to decontaminate**

   The cell was designed so that the cell base could be easily separated into two parts for cleaning. This is a significant feature in the design. The least accessible regions, the 8 mm ports for the connectors and central collecting channel, can be visually inspected and are easy to access with a small bottle brush should they become contaminated. The O-ring in the base is easy to remove and replace.

8. **Quick to assemble and use**

   A sample can be cut from an item of CPC with a 25 mm wad punch in a couple of seconds. There is an unavoidable delay between weighing a sample and measuring its thickness. Placement of the sample in the cell, assembly of the cell and setting it in the clamping frame with a torque wrench took less than 10 seconds. No retightening of the clamping bolts is necessary. Connection of the pneumatic lines by hand took seconds, but it was necessary to cut the lines to within 1 cm of the desired length.

9. **Resistant against solvents, acids, alkalis**

   The cell construction was of brass, for ease of machining. This material would give good resistance to most common solvents, but limited resistance to corrosive chemicals. The cell (or at least the simple tubular body) could be made of stainless steel or even a stock section of glass or quartz tube. This would add to the cost, and in the case of glass, reduce ruggedness, but add to the chemical resistance and permit the sample to been viewed during testing.

10. **Little training in use to get reproducible results**

    The Griffith Mk2 cell was almost as easy to use as the Griffith cell that has been successfully used by hundreds of undergraduate students with little training. No controlled trials were performed to determine reproducibility under these conditions as stain tubes and washing-up glove samples presented poorly controlled variables.

11. **Rugged – undamaged by a 1 m drop test onto a hard floor.**
The cell appeared to be undamaged by drops from 1 m onto a polymer coated concrete floor. There would be some potential to damage the seal on the cell body if one another part of the cell or something hard cut into the brass surface of the body, but repair on a lathe or with sandpaper would be possible. The seal on the cell base was protected by a lip.

12. **Replaceable components are “off the shelf”**
   The O-rings and the pneumatic connectors are replaceable at a low cost from many suppliers.

13. **Cheap and easy to fabricate**
   The cells were designed to be easy to fabricate, with the only critical dimension being the fit of the two parts of the cell base to form the annular slit to deliver the circumferential collecting flow. The fit could be readily achieved on a simple lathe.

14. **In the public domain (no copyright or royalty)**
   The cell design is in the public domain.

15. **Can be used in the field**
   The cell can be used in the field with a single cell clamp, a personal sampling pump and either a field detector (such as the HNU 101 PID used in this research) or stain tubes as integrating detectors.

16. **Capable of being used for intermittent exposure testing**
   Chapter 8 discusses a modification of the cell, the Griffith Mk2 Intermittent exposure cell that made it suitable for use with for intermittent exposure testing.

17. **Adequate sample size to prevent edge effects**
   A simple model from Crank (1975) of the effect of sample diameter demonstrated that no edge correction was required for any of the permeation cells used.

**SECTION 4.11 CONCLUSIONS**

The conclusions in this chapter about continuous exposure cells is supplemented by more detailed studies on the effects on operational parameters such as the collecting flow rate and flow pattern in Chapter 5.

4.11.1 **Cell Validation**
- The main finding of this chapter is that the Griffith cell and the Griffith Mk2 cell are valid alternatives to the ASTM cell, in accordance with the ASTM F739-1996 validation criteria.
- The Griffith cell and Griffith Mk2 cell are also equivalent to each other, using the precise permeation data generated in this research.
• The difficulty in producing reliable normalised breakthrough time data at a low permeation rate impedes the automation of permeation testing. This difficulty is overcome by the use of Lag Time.

4.11.2 Design Criteria
• Comprehensive design criteria to produce an “ideal” two-chambered permeation cell were developed. However, there is still a need for further investigation of the collecting flow regime next to the test sample, both experimentally and computationally, to determine the thickness and nature of the boundary layer that must exist. The author did not have the expertise or the laboratory facilities to pursue this matter.
• The Griffith Mk2 cell has been shown (Chapter 5) to satisfy most of these design criteria, particularly a good flow regime and almost zero back pressure on the test sample over a wide range of collecting flows. The criteria of low cost, ruggedness and ease of fabrication were also satisfied. Constraints of cost and simplicity prevented it from being able to be used with corrosive chemicals and solid collection media and limited its use with solid challenge chemicals. Replacement of the simple cell body with stainless steel or glass would allow corrosive material to be tested.

4.11.3 Permeation Indices and Number of Measurements
• The nBT measurement at 0.1 μg cm\(^{-2}\)min\(^{-1}\) places considerable constraints on test systems with multiple cells sharing a single detector as carry over between cells limits the analytic detection limit. It was found that to measure the nBT permeation rate of 0.1 μg cm\(^{-2}\)min\(^{-1}\) with acetone, only one cell could be measured at a time.
• The problems in establishing an index relating to breakthrough with multiple cell systems were entirely overcome with the use of Lag Times due to the lesser dependence of LTs on detection limits. LT is a much more precise measurement than BT, as it is derived from the extrapolation of permeation data well in excess of the nBT permeation rate of 0.1 μg cm\(^{-2}\)min\(^{-1}\). Both LT and BT are similar times and are indicative of significant amounts of permeant appearing on the “inside” of a CPC sample. BT and LT are different, but should provide similar rankings of CPC choices.
• Trials with toluene vs single and double dipped PVC gloves as a worst case, and acetone vs reference neoprene as a best case, indicated that SSPR could adequately discriminate (p = 0.05, Ansell PVC “worst case” choices) between samples with the
three measurement recommended by ASTM F739-1996. With uniform samples (reference neoprene), BT could only discriminate a 30% difference. LT performance was better than SSPR in the best case scenario but not as good as SSPR in the worst case scenario where 36 measurements were required to discriminate a 30% difference.

- Because LT is suited to testing with multiple cell systems, it is a much more precise indicator of CPC performance than BT, but as little LT data have been published, it would serve to supplement rather than replace BT in ranking CPC choices.

4.11.4 Other
- A very rigid frame is required to clamp multiple cells with negligible bowing.
CHAPTER 5. EFFECTS OF OPERATIONAL PARAMETERS ON PERMEATION

SECTION 5.1 AIM

This chapter reports the use of the Griffith Mk2 cell to investigate operational parameters that have been little explored or are contentious. These operational parameters include:

- those that could affect permeation were the pattern of the collection flow, the collection flow rate and the depth of liquid challenge chemical over the test sample; and
- those that could affect the interpretation of the permeation data were estimates of sample thickness and the pre-treatment of the test sample.

SECTION 5.2 EFFECT OF COLLECTING FLOW PATTERN ON PERMEATION

5.2.1 Introduction

To justify the assumption of zero concentration of the permeant on the "inside" surface of the CPC sample during permeation testing, permeant must be immediately removed from the surface. The thicker the boundary layer that contains this permeant, the less it may be assumed that the permeant concentration next to the CPC is zero. Removal of this boundary layer over the entire "inside" surface of the test sample would require not only that there is a disrupting flow of collecting gas over the surface, but that the whole surface receives this flow with no pockets of stagnation.

5.2.2 Collecting Flow and Cell Design

A formal discussion of fluid dynamics is beyond the scope of this work and a qualitative description of the flows is given. For a circular test sample there are a number of collecting flow regimes that can be created. The simplest is a central jet with collection of the carrier fluid after it has swept the test sample, but there are at least two regions of possible flow stagnation. The centre of the jet is potentially stagnant, as there is radial symmetry to any circular jet. In practice, there is sufficient turbulence from the jet to ensure any stagnant point moves sufficiently to negate stagnation at this central point. A second stagnant region is at the outer circumference of the test sample. The flow slows here as it moves radially outwards. The flow pattern also becomes more complex as it nears the cell wall and must change direction, but the flow will curve rather than make
an abrupt change. This outer region forms a significant proportion of the area of the sample and may experience some build-up of permeant, particularly where the flow changes direction near the walls of the cell. This would reduce the average permeation rate over the sample and result in an overestimation of the barrier properties of the CPC. This pattern would be expected in the ISO cell, as shown in Figure 41, with potential stagnation points on the surface of the sample at "A" and "B".

![Figure 41](image)

**Figure 41 Expected flow pattern and potential stagnation points, A and B in ISO cell**

An alternative approach is to produce a flow pattern starting at the circumference of the test sample and moving inwards towards the centre of the sample. An annular flow could be achieved with a series of holes at the circumference of the cell or by an annular slit. In creating the Griffith Mk2 cell, a number of designs were considered, including a circumferential array of jets, to produce a radial inwards flow. These were rejected as they either required too much precision machining or would be difficult to decontaminate. The collecting part of the cell (the cell base and collecting ring) was eventually fabricated in two simple parts, a cell base and a flow distributing ring, as shown in Figure 42.
Figure 42 Griffith Mk 2 cell flow pattern (connectors and cell lid removed)

The flow hits the test sample at a high velocity (200 km hr\(^{-1}\) for a 0.1 mm annular slit for a flow rate of 10 Lpm). However, the distance of the jet from the edge of the sample is so small that the sample does not distort. The test sample as depicted in Figure 43 may be considered to be a beam for small deflections due to the jet. The bending moment at a point on a cantilevered beam is proportional to the square of the distance along the beam.

Figure 43 Effect of circumferential placement of flow into collecting volume

If the inlet jet hit the centre of the sample at "B", 10 mm from the edge of the sample, it would produce a bending moment of 10 x 10 or 100 units. The same jet 0.1 mm from the circumference at "A", produces a bending moment of 0.1 x 0.1 or 0.01 units, 10,000 times less. Further, when the flow at "A" turns horizontal, its channel has expanded..
from 0.1 to a nominal 1.0 mm, so the flow impedance is less, there is little back pressure and the flow is now parallel to the sample. A flow between the cell base and sample plates should actually produce a slight pressure drop due to the Bernoulli effect (Halliday and Resnick, 1970), so the mechanical effect of the flow on the sample should be minimal. This aspect of the design was determined empirically.

The collecting flow velocity at any point radially in the collecting volume is determined by the volume flow, depth of the collecting volume and the distance from the centre of the cell. Thus the flow accelerates as it moves inwards towards the centre of the cell. This ensures better scrubbing of permeant from the entire surface of the sample and increasing turbulence, reducing the possibility of stagnation at the centre of the test sample. Once the flow has reached the centre of the cell, it exits down the large (8.8 mm) central channel and out of the cell. If the chemical detector only samples this effluent flow rather than intercepts it, then there should again be a very low back-pressure on the test sample, even at gas flows of 10 Lpm or greater.

The small (~0.1 mm) size of the annular slit acts as a high impedance to the collecting flow and ensures that the collecting gas or liquid is supplied evenly around the annulus. A larger slit of about 0.5 mm was tested and produce an less even annual jet. The size of the slit was determined by the quality of the lathe – a much smaller slit could not be reliably machined and remain uniform around the collecting volume. The efficacy of the slit to produce a uniform flow was demonstrated with a hot wire anemometer (Alnor, 0-30 m s\(^{-1}\)) at moderate slit velocities (<30 m s\(^{-1}\)). The metering valve and the annular slit were the two major flow resistances for the collecting medium in the test rig, and as both were upstream of the sample, they did not pressurise the sample. Perkins and You (1992) had to reduce the flow through a MIRAN closed loop calibration pump to 4 Lpm with an ASTM cell to avoid "pressure pulsation effects" found at 8 Lpm. This demonstrates that high flow rates can lead to vibration of the test sample, as well as bulging from pressure imbalance.

5.2.3 Reynolds Number Calculations in Griffith Cell
If likely regions of stagnation are identified and the flow regime is shown to be turbulent in those regions, then it is assumed that adequate, turbulent flow will be produced over the rest of the surface of the sample.
The Reynolds number of a fluid flow gives a dimensionless ratio between the inertial and viscous forces. Tripping a flow over a flat plate at a low Reynolds number of 360 can result in a turbulent flow (Gough et al., 1996), though the generally accepted figure for the transition from laminar to turbulent for flow in pipes is 2,300. Once turbulent flow has tripped, it will continue to be turbulent for some distance into a region where the Reynolds number is somewhat lower.

The Reynolds number (Re) in a flow may be expressed as a relationship between the linear fluid velocity $U$, the appropriate dimension $L$, and the kinematic viscosity $\eta$.

$$Re = \frac{UL}{\eta}$$

................................ Equation 9 Reynolds number

Reynolds numbers for the Griffith cell were calculated using the following characteristic lengths.

- the inlet diameter (3.7 mm); and
- The gap between the test sample and the base of 1.12±0.47 mm. The large uncertainty was related to the precision in machining this particular dimension.

If there is stagnation in the collecting volume of the Griffith cell, then the region, midway between annular jet and the centre of the cell, labelled "X" in Figure 44, would be the region most likely to be affected. Consequently, the flow velocity at "X" was taken as a point for calculation of the Reynolds number at the sample and taken as the

Figure 44 Possible region of stagnation "X" in the Griffith cell

If there is stagnation in the collecting volume of the Griffith cell, then the region, midway between annular jet and the centre of the cell, labelled "X" in Figure 44, would be the region most likely to be affected. Consequently, the flow velocity at "X" was taken as a point for calculation of the Reynolds number at the sample and taken as the
worst case. A reasonable degree of radial symmetry of the flow was assumed in calculating the flow velocity at "X". This assumption is examined in the flow visualisation experiments in subsection 5.2.4.

The Reynolds numbers at the inlet port were also calculated, using the diameter of the inlet port as the characteristic length. This calculation was necessary to demonstrate that similar or more turbulent flow regimes existed upstream of the collecting volume. If the inlet flow is laminar, then turbulence would be less likely in the collecting volume.

Data from Kundu (1990) for the viscosity of air (air and nitrogen are similar) were used to calculate the Reynolds numbers "Re" for the Griffith cell at different collection gas flows in Table 12.

<table>
<thead>
<tr>
<th>Flow (mL min⁻¹)</th>
<th>Inlet jet (Re)</th>
<th>Midway &quot;X&quot; (Re)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>363</td>
<td>432</td>
</tr>
<tr>
<td>100</td>
<td>655</td>
<td>860</td>
</tr>
<tr>
<td>250</td>
<td>1,637</td>
<td>2,150</td>
</tr>
<tr>
<td>500</td>
<td>3,274</td>
<td>4,300</td>
</tr>
<tr>
<td>7500</td>
<td>49,110</td>
<td>64,495</td>
</tr>
</tbody>
</table>

As demonstrated in Table 12, the flow is turbulent throughout the collecting volume of the Griffith cell for moderate flow rates (at "X", Re > 2000 for flows greater than 250 mL min⁻¹), so no stagnation or significant boundary layer problems would be expected. At 500 mL min⁻¹, the flow rate used in the validation experiments, the flow in the collecting volume is highly turbulent. A more detailed examination of the disruption of boundary layers in the Griffith cells and other cells is beyond the scope of this work and could be the subject of further work.

5.2.4 Flow Visualisation Experiments

Flow visualisation was performed to identify regions of stagnation and to verify that the radial symmetry of the flow, assumed in the Reynolds numbers calculations, was valid.

The flow through the Griffith cells at their nominal design flow of 500 mL min⁻¹ produced a clearance that was too fast to be visualised with smoke. Flow velocities scaled for use with water as the collecting fluid enabled visualisation of the flow with dye injected into the water.
The Griffith cell and the Griffith Mk2 cell were both prepared by painting the collecting area with typing "whiteout" to provide contrast to the dye. The cells were then placed in a single cell frame modified with a hole in the bottom. The body of the cell was removed and the sample substituted with a thick plastic disc sealed with a thin neoprene gasket. The assembly was held inverted by a wooden frame. In this inverted position it was possible to see a red dye introduced into the cells with a 10 mL plastic syringe connected to plastic tubing (Figure 45).

![Flow visualisation, Griffith Mk2 cell](Image)

The top of the frame was painted matt black to assist in imaging the flows. A video camcorder was mounted above the assembly, pointing downwards and a "Post-It" label (3M) allowed the flow details to be recorded on the video image.

Water was introduced through a "T" connector and red dye injected into the flow through another arm of the "T" connector. To ensure a concentrated bolus of dye, a piece of narrow bore plastic tubing (from a Technicon Autoanalyser) was attached to the needle to release the dye directly into the collecting volume of the cell. Frames from the video recording were grabbed using the frame grabbing capabilities of a video editing facility (FAST Video Machine Lite, FAST Electronics, [http://fast-multimedia.com](http://fast-multimedia.com)). The images were cropped using a graphics editing program (PhotoShop 2.5 SLE, Adobe, [http://www.adobe.com](http://www.adobe.com)) and the red colour saturation was digitally enhanced to emphasise the dye. To permit better visualisation of the dye, the red areas were outlined with a drawing tool.
The water flowed through the cell at a scaled rate of 1/15th that of air or nitrogen. The flow rate was determined by the timed filling of a beaker. A syringe was arranged to introduce water-soluble red dye (as used with water tables) into the cell. A small finger tap on the syringe proved to be adequate to inject a visible bolus of dye without affecting the flow.

A similar experiment was performed with the ASTM cell, but the transparency of the glass made direct visualisation possible. A black piece of PVC gave a non-reflecting background and a halogen lamp illuminated the cell to maximise contrast of the dye. Flow through the collecting volume in both possible directions was examined.

![Flow visualisation, reverse flow, ASTM-F739 cell](image)

5.2.5 Results of Flow Visualisation Experiments

**Griffith cell flow pattern**

At "450" mL min\(^{-1}\) (30 mL min\(^{-1}\) water flow) a small bolus of dye distributed evenly over the sample and collected in the collecting ring. The area inside the collecting ring became clear and the red fluid in the collecting ring moved to the outlet. The same occurred at "100" mL min\(^{-1}\) (6.6 mL min\(^{-1}\) water flow), but with some initial loss to the outlet. The bolus took 10 seconds (equivalent to less than 1 second with nitrogen) to reach all points of the collecting ring in the expected areas of stagnation, with some asymmetry.
Figure 47 Griffith cell water flow at 24 mL min\(^{-1}\) (360 mL min\(^{-1}\) air)

Figure 47 shows sequential frame grabs of the water flow in the collecting region of a Griffith cell at a water flow of 24 mL min\(^{-1}\). Frame "A" shows the bolus of dye distributing itself over the collecting area from the centre of the cell. There was some asymmetry towards the collecting port but there appears to be sufficient radial symmetry to justify the flow velocities used in the Reynolds number calculations in section 5.2.3. Frame "B" shows the dye evenly distributed over most of the collecting volume. Frame "C" shows most of the dye almost gone, except for a small amount in the collecting ring opposite the collecting port.

With increased water flow (480 mL min\(^{-1}\)), the appearance and disappearance of the bolus was almost immediate, but pronounced swirling of the flow occurred. Flow along the collecting ring in an anticlockwise pattern was evident in all three frames in Figure 48. There were no stagnant regions.

Figure 48 Griffith cell water flow at 480 mL min\(^{-1}\) (7200 mL min\(^{-1}\) air)

Furthermore, at all the flow rates tested, the dye did not flow directly to the collecting port, but flowed evenly to the collecting ring and then to the collecting port. Thus, the assumption of reasonable radial symmetry to calculate the flow regime at position "X" in Figure 44 was supported.

Griffith Mk2 cell flow pattern

The flow through the collecting volume of the Griffith Mk2 cells was more uniform than the flow in the Griffith cells. Water flow at 320 mL min\(^{-1}\) is shown in Figure 49.
In frame "A", the intensity of the dye was radially symmetric, and the flow meets in the centre of the cell. In Frame "B" which follows "A", there was some asymmetry, as there was residual dye from the distributing ring under the annular slot. As the dye entered the distributing ring from the top of the figure, some asymmetry could be expected in the clearance pattern of a bolus of dye. This does not suggest that the uniform flow itself changes. There was no possibility of stagnation.

**ASTM cell flow pattern**

Flow patterns in the collecting side of the ASTM cell were not well defined in either of the two directions and an example of the pattern is shown in Figure 50.

As the critical area was the region next to the test sample, dye was released in this area at "A". The incoming flow at "C" gradually displaced the dye to the region "B". Some of the dye persisted in the filling neck of the cell. The flow pattern was not uniform in

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4 The ASTM F739 cell is available in two sizes and in three configurations (ASTM F739, 1996), for liquid test chemicals, closed loop test and gaseous test chemicals. The configuration for liquid test chemicals – as illustrated in ASTM F739 1996 was used in this work, with a “replaceable stirring rod to allow continuous monitoring with air or nitrogen”. The liquid test chemical ASTM F739 cell used in this work was made by a local scientific glass company using this illustration for guidance. It was not clear which was the entry port and which was the exit port, so the port that directed the gas flow onto the sample was used.
the collecting volume. Stagnation may have occurred next to the sample but the technique was not sensitive enough to detect this in the deep collecting volume of the ASTM cell. There was some short-circuiting of the flow from the stirrer port "C" to the cell exit port "D". The regions of stagnation in the collecting side of the ASTM cell are shown in Figure 51.

![Figure 51 ASTM cell flow stagnation zones](image)

As the collecting volume of the ASTM cell was much larger than the corresponding volumes in the Griffith cells, it was possible to perform flow visualisation tests with smoke with the ASTM cell tests. Chemical smoke from a smoke tube (Drager) and air flowing through the cell gave qualitative results that appeared similar.

### 5.2.6 Discussion of Flow Visualisation Experiments

The flow visualisation experiments with the Griffith cell indicated that a turbulent flow over the surface of the sample would have removed the permeant adequately at the flow rates (500 mL min⁻¹) used in the validation experiments against the ASTM cell.

The collecting ring in the Griffith cell (Figure 44) performed its designed role in permitting a radial flow to move to the outlet port at all flow rates, by creating a channel for the axial flow to drain. Similar tests on the Griffith Mk2 cell showed a superior flow pattern with almost complete radial symmetry of the collecting flow. Tests with the ASTM cell demonstrated significant regions of stagnation with the flow through the cell in either direction, though stagnation was not noted near the test sample, as the collecting volume was too deep.
Clearance of dye can be modelled using the Dilution Equation (Buonicore and Davis, 1992). This may be expressed in terms of the time \( t \) for the concentration in the collecting volume to reduce from \( C_0 \) to \( C \).

\[
t = \frac{kV}{Q \ln \left( \frac{C}{C_0} \right)}.
\]

.......................... Equation 10 Dilution equation

where

- \( k \) mixing coefficient
- \( V \) collecting volume of the cell
- \( Q \) flow rate through the cell
- \( C_0 \) initial concentration in the cell
- \( C \) concentration in the cell after \( \Delta t \)

ASTM F739-1996 suggests a minimum collecting flow rate of 50 mL min\(^{-1}\). At this flow rate, and \( C/C_0 = 1\% \), \( k = 1 \) (ideal mixing) and \( V = 100 \) mL the clearance time \( t \) for the ASTM cell was calculated to be 9 minutes 13 seconds. Stagnation in ASTM cells using smoke tubes was reported by Anna et al. (1998), but not mapped. They found that at a flow rate of 50 mL min\(^{-1}\) the smoke cleared in "approximately 9 minutes", confirming that most of the flow in the collecting volume at this flow rate that could be equated to ideal mixing. However, Anna et al. also noted additional smoke came from the cell when the flow rate was increased, indicating that pockets of stagnation existed.

The flow pattern in ASTM cells is complex and can be represented by a multi-compartment model with at least three compartments (Figure 52). Permeant is exchanged between the main collecting volume and large stagnant regions in a complex, flow rate dependant manner. Permeant at the surface of the sample diffuses into the main collecting volume.
In this research, less than ideal mixing was also observed for the ASTM cell using water and dye, and major regions of stagnation were identified. Anna et al. (1988) also noted stagnation, and additional clearance of smoke injected into the cell when the flow rate was increased. From this and flow rate - permeation rate studies, a minimum flow rate of 500 mL min⁻¹ rather than the recommended maximum of 150 mL min⁻¹ was suggested by Anna et al. (1988).

Another method, such as a dye of low volatility coating the test sample, might reveal regions of inadequate flow near the surface of the test sample. The use of tracer gases, or dye in water, with a spectrophotometer containing a flow-cell, would put quantitative estimates on the degree of mixing in the cell at different flow rates. However, this would not necessarily indicate that the mixing was uniform throughout the cell at low flow rates.

### 5.2.7 Transient Response of ASTM F739 Cell to Collecting Flow Changes

As shown in subsection 5.3.3, changing the collecting flow rate above a minimum flow rate does not alter the SSPR. However, it was noted that when a step change was made to the collecting flow rate, the measured SSPR took a significant time to settle to close to its original value. This effect increased with the cell dead space and was greater at low flow rates.

The settling of permeation rates in response to step changes in collecting flow is shown in Figure 53 for the ASTM F739 cell as it demonstrated the greatest effect with its large collecting volume and flow limitations due to port size.
Figure 53 Settling pattern of ASTM F739 cell with a change of collecting flow rate

The lower plot shows the collecting flow rate normalised to the exposed area of the test sample (mL min\(^{-1}\) cm\(^{-2}\)). This was stable to within 1.3% and was stepped from 95 to 108 to 148 mL min\(^{-1}\) cm\(^{-2}\). The corresponding absolute flow rates are shown in brackets. The upper plot shows the measured permeation rate (\(\mu\)g cm\(^{-2}\) min\(^{-1}\)) as the system settled to the true SSPR. In the first minute, the PID data were off-scale.

As the PID was off scale before the flow was increased from 95 to 108 mL min\(^{-1}\) cm\(^{-2}\), the effect of changing flow rate on the recorded permeation rate cannot be examined in this region. In region "A", the SSPR settled from 245 to 235 \(\mu\)g cm\(^{-2}\) min\(^{-1}\). The transitory response or peak at "B" is due to the residual concentrated permeant collected at a low flow rate being detected. (The reason peak “B” was measured, but the PID was off-scale earlier is that the calculated permeation rate is calculated from the solvent concentration, the collecting flow rate and the area of the test sample – a moderate PID reading at a high flow rate gives a high permeation rate. A near off-scale PID reading at a low flow rate gives a lower permeation rate.) The time this bolus takes to disappear is now used like a tracer gas to determine the degree of mixing in the cell. The change in "B" at 2190 mL min\(^{-1}\) from 310 to 264 \(\mu\)g cm\(^{-2}\) min\(^{-1}\) in 4 seconds corresponds to \(k = 6.6\). Thus the actual mixing in the ASTM cell was demonstrated to be less than ideal (ideal: \(k = 1\)).
If the ASTM cell is viewed as a simple volume then the dilution equation can be used to estimate the degree of mixing.

SECTION 5.3 EFFECT OF COLLECTING FLOW RATE ON PERMEATION

Studies of the collecting flow rate complement the studies of collecting flow pattern. If the flow pattern is designed to disrupt boundary layers next to the test sample and prevent regions of stagnation occurring, then the flow rate at which this efficiently occurs may be directly verified by permeation rate experiments at different flow rates. As the flow past the detector could affect the response of the detector and fluctuations in flow rate would permit transient conditions to exist, these factors were also investigated.

ASTM F739-1996 recommendations for the gas collecting flow rate for the ASTM cell are 50 to 150 mL min\(^{-1}\). If the chemical flux through the test sample is proportional to the exposed area of the sample, then the Griffith cell flow would have to be scaled by 4 to give the same concentration in the effluent flow - between 12 and 35 mL min\(^{-1}\).

If stagnation and boundary layer effects were significant, then increasing the flow rate through the cell would tend to both disrupt stagnant pockets and reduce the thickness of boundary layers. Disrupting stagnant pockets of permeant would mainly produce a transitory increase in concentration of permeant in the effluent flow, but reduction in boundary layer thickness would produce a real increase in permeation rate. Once the true permeation rate is measured, a plot of permeation rate against collection flow rate should give a horizontal line. A similar approach was taken by Anna et al. (1988) who doubled the flow rate until the measured SSPR did not change. This was used to determine the minimum flow rate to determined the true SSPR.

However, before experiments on the effect of collecting flow rate on permeation could be performed, it was necessary to demonstrate that the flow rate past the PID did not affect its response.

5.3.1 Effect of Flow Rate Past Detector

To determine the response of the PID to flow, 10 µL of acetone was injected into a Tedlar sampling bag containing 4 L of nitrogen. The bag was placed in a sealed plastic bucket and pressurised with compressed air (Figure 54) via a metering valve.
Adjusting the metering valve V1 changed the external pressure on the Tedlar bag and the rate at which the standard atmosphere from the bag passed through a calibrated mass flow transducer Q (Honeywell AW5100), and then past the PID. The flow past the PID was regulated by the precision metering value V3, connected to the house vacuum.

The pressure in the bucket was also monitored by the pressure meter P, to determine when the Tedlar bag was deflated, as a sharp increase in pressure in the bucket would be expected as the bag became empty. An effect noted after partial deflation of the bag was that the flow rate signal contained spikes that corresponded with crackling noises from the Tedlar bag. These were thought to relate to the collapse of apexes formed in the Tedlar bag as it crumpled. The flow spikes did not affect the response of the PID. In these trials, the flow into the PID itself was set at 50 mL min⁻¹, so collecting flows past the PID that were less than this resulted in the PID sucking in room air.
Figure 56 Response of PID to collecting flow rate

The horizontal line in Figure 56 clearly shows that the flow past the PID does not affect the response of the PID, particularly at high flow rates when a small pressure build-up could possibly alter the sampling flow rate through the PID. Any change in the SSPR through a sample in a permeation cell with collection flow can therefore be attributed to the collection flow rate, not the PID.

5.3.2 Effect of Collecting Flow Rate on Measured Permeation Rate

Four cells were used in this experiment – the Griffith Small cell, the Griffith cell, the Griffith Mk2 cell and the ASTM cell. Though other tests were not performed on the Griffith Small cell, it was included in this experiment, as it was known that at low collecting flow rates, the PID would be off scale for the other cells. Flow rates were varied from 100 mL min$^{-1}$ to over 7,000 mL min$^{-1}$ during a test using reference neoprene challenged with acetone.

Initial collection flow rates were set as for the validation experiments for the Griffith cell (500 mL min$^{-1}$) and ASTM cell (2000 mL min$^{-1}$), and flows scaled on exposed sample area for the Griffith Small cell (100 mL min$^{-1}$) and Griffith Mk2 cell (500 mL min$^{-1}$). The cells were then run until steady state conditions were well established.

A metering valve for the cell was altered in stages from a lowest rate possible, determined by the upper limit of the PID, up to 10,000 mL min$^{-1}$ that was limited by the
range of the mass flow sensor. The PID went off scale with all the cells before the flow rate dropped to 50 mL min\(^{-1}\), the sampling flow rate into the PID. To guide the adjustments of the metering valve, Visual Basic code was written that allowed the response of the detector multiplied by the flow rate (effectively the permeation rate) to be plotted against the flow rate. If the flow rate had no effect on permeation, then a horizontal line would be expected, once the system had settled down to a new flow rate.

### 5.3.3 Results on the Effect of Collection Flow Rate on Measured Permeation Rate

Changing the collection flow rate over a wide range for the four cells made no significant difference to the steady state permeation rate as shown in Figure 57.

![Figure 57 Effect of collection flow rate on SSPR](image)

Much of the scatter at low collecting flow rates is due to the long settling time of the cell after increasing the flow rate. Only one set of data did not give an off scale reading on the PID below 400 mL min\(^{-1}\), that for the Griffith Small cell. In this data, the PR was greatly reduced at 63 mL min\(^{-1}\). At 157 mL min\(^{-1}\), the Griffith Small cell returned a "normal" PR (expanded view in Figure 58). The ASTM cell was not shown in Figure 58 as the PID was off scale at a normalised flow rate of 1000 mL min\(^{-1}\) cm\(^{-2}\). In this trial, the Griffith cell appears to give consistently lower permeation rates than the other cells, but this appears to be within experimental error.
Figure 58 Effect of low collection flow rates on SSPR

It is clear that at very low flow rates the permeation rate drops perhaps due to the lack of disruption of the boundary layer at low flow rates. However, only the Griffith Small cell permitted such measurements, as its sample area was small enough to permit the PID meter to remain on scale at low flow rates. Some data at lower flow rates had to be discarded on analysis, as the permeation rate had not sufficiently settled after changing the flow.

The effects of flow on permeation with all the cells was directly compared by plotting the permeation rate with the collecting flow rate normalised to the exposed area of the sample in each cell, on the premise that the amount of acetone permeating a sample is proportional to the area of the sample. This normalised plot is shown in Figure 59.
Figure 59 Effect of normalised collection flow rate (mL min\(^{-1}\) cm\(^{2}\)) on SSPR

The flow rate experiments do indicate that the effects of collecting flow rate for normalised flow rates over 150 mL min\(^{-1}\) cm\(^{2}\) were small (<2.5% over the range). However, as indicated in Figure 59, a trend of increasing permeation rate with flow may exist at a normalised flow rate of less than 1000 mL cm\(^{-2}\) min\(^{-1}\) for the Griffith cell and perhaps the Griffith Mk2 cell. At very low flow rates, there was evidence that the flow in the collecting volume was insufficient to remove all the permeant in the Griffith Small cell. This would be expected with any two-compartment cell and a further experiment is warranted to determine this limit for a variety of cells. This would use either a different detector or a diluted flow to the detector. Diluted flows were not used here, as it would have required a second flow sensor to monitor the diluting flow.

At low flow rates, the upward curving of the plots in Figure 59 was almost certainly an artefact of insufficient settling time for the PID. The upward curve was most apparent with the ASTM cell with a large (100 mL) dead volume, but least apparent with the Griffith Mk2 cell with almost no dead volume. To the cell dead volume must be added the volume of the plumbing downstream of the cells, including the volume of the ion chamber in the PID.

In developing the timing for the GloveTest system, the exponential setting time from one Griffith Mk2 cell to another was found to be about 20 seconds with a collecting
flow rate of 500 mL min\(^{-1}\) This represented a step change in the acetone concentration presented to the PID. A similar response is seen in the raw data used in these flow experiments. The data for the ASTM cell is shown in Figure 60.

**Figure 60 Transient response of GloveTest system with ASTM cell**

In Figure 60, the ASTM cell with acetone and reference neoprene has been brought to steady state conditions. The flow rate (as a flow rate per unit sample area) is increased in steps from 100 mL min\(^{-1}\) cm\(^{-2}\) to 700 mL min\(^{-1}\) cm\(^{-2}\). At each increase of flow, the bolus of permeant generated at a lower flow rate produces a transient peak. The circle shows the almost immediate response of the system to the change in concentration in the collecting flow, but a much slower return to steady state values due to the dead volume of the entire system. At about 160 seconds, the flow is decreased, producing a bolus of permeant generated at a lower apparent permeation rate, showing the reverse occurs. The time for the permeation rate to return to steady state conditions appears to decrease with increasing flow rate, as expected, but has not been quantified.

The normalised collection flow rate used in the validation experiments with the Griffith cell and ASTM cell was 150 mL min\(^{-1}\) cm\(^2\), as shown in Figure 59. Based on these results, this normalised flow rate is satisfactory but towards the bottom end of the acceptable flow range.
The work done by Anna et al. (1998) found that the recommended flow rates for the ASTM cell underestimated the SSPR, as they were too low to remove the permeant efficiently. This result cannot be generalised to all chemical permeant combinations as Anna et al. demonstrated that different chemical-polymer combinations needed different collecting flow rates to permit an estimation of the true SSPR. However, the advice of Anna et al. to increase the collecting flow rate until a true SSPR is achieved has great merit.

In summary, the effect of collecting flow on permeation at the flows used, and for the acetone-reference neoprene tested, was not significantly affected by the flow rate. A further experiment is warranted, supported by the work of Anna et al. (1998) to determine the lower flow limits of the cells, for a range of solvents.

SECTION 5.4 EFFECT OF COLLECTING FLOW RATE ON CELL PRESSURE

Pressure build-up in cells can not only stretch and thin a sample but may also change the orientation of polymer chains, and thus change the barrier properties of the sample. Several experiments were conducted to determine this pressure build-up in cells with different collecting flow rates, and with different downstream attachments to the cells.

The GloveTest rig was designed so that the main pressure drops in the system were upstream of the cell, but it was still necessary to measure the solvent concentration downstream from the cell. The temperature of the effluent gas was also routinely measured with a solid state temperature sensor inserted in some 6 mm tubing. These elements downstream of the cell still had the potential to produce a backpressure on the test sample.

The effect of collecting flow rate in the cells in creating backpressure was measured in one experiment. Another experiment related the static pressure in the cells to distension of the sample, for both new and used reference neoprene samples.

5.4.1 Flow-Pressure Experiment

To measure the pressure build-up in the cells with collecting flow rate, different approaches were needed for the different cells. For the Griffith Mk2 cell, a hypodermic needle attached to a micro-manometer (±1 Pa) pierced the sample to measure the pressure in the collecting volume. The needle was held steady by a retort stand and the
cell held in the flow visualisation test jig. For the ASTM cell, the pressure imbalance was measured via the stirring port on the collecting volume. The micro-manometer and the flow through the collecting volume were logged.

### 5.4.2 Sample Distension Experiment

A jig was constructed to hold half of the ASTM F739-1996 cell with the sample clamped against a hole the size of the exposed sample in a piece of thick plywood.

![Figure 61 Jig for measuring distension of test sample](image)

A digital calliper (readability 10 μm) was clamped to the jig to measure the distension of the sample when the cell was pressurised with nitrogen. A similar arrangement was made for the Griffith Mk2 cell. The nitrogen pressure in the cell was adjusted via needle valves on the inlet and outlet ports to the cell. A digital manometer, P (0-15 kPa) was attached to the cell to measure the static pressure in the cell.

New and used samples of reference neoprene were tested in the ASTM cell and a new sample was tested in the Griffith Mk2 cell. The used sample had been exposed to acetone for several weeks in the ASTM cell, and the discolouration of the residual acetone indicated the leaching of material from the sample. This discolouration was observed after even a short trial.

The digital callipers were set to zero when the pressure in the cells were zero. This was difficult to judge as the act of clamping the test sample causing a slight bowing of the sample. For these tests, the clamping was light as a perfect seal was not required. The "used" sample was not flat like the new samples and there were greater uncertainties in determining the point for zero distension.

When the pressure inside the cell was set at a particular value, the depth probe on the digital callipers were moved until it just touched the surface of the sample.
Determination of this point was assisted with bright illumination from a quart halide spot-lamp placed at a distance of two meters to minimise heating of the sample. The uncertainty in the placement of the digital callipers was estimated to be 0.05 mm.

5.4.3 Results of Flow-Pressure Experiments

**Pressure upstream of the cells**

To demonstrate the effect of the high flow impedance of the annular slit in the Griffith Mk2 cell only data for the Griffith Mk2 cell and ASTM cell were collected. The plots are shown in Figure 62. The data for the Griffith Mk2 cell were limited by the upper range of the pressure sensor, but the ASTM cell data was limited by the upper rage of the mass flow sensor.

![Figure 62 Pressure buildup upstream of cells with collecting flow rate](image)

The impedance to flow in the Griffith Mk2 cell was due almost entirely to the designed pressure drop in the annular slit. This was upstream of the sample, so did not affect the sample. The pressure drop with the ASTM cell was due to the stopcocks and narrow glass ports to the cell. The impedances in the port on the downstream side of the ASTM cell would lead to the sample being pressurised. The data to support this view is given in Figure 58.
**Griffith Mk2 cell flow-pressure plots**

The Griffith Mk2 cell was tested with various downstream attachments to determine the effects of these attachments on the pressure build-up in the cell. These downstream attachments were

- No attachments – the Griffith Mk2 cell alone,
- PID,
- PID plus temperature sensor, and
- GloveTest rig, including poppet valve, PID and temperature sensor.

These pressure-flow plots are shown in Figure 63, along with a plot for the ASTM cell.

![Figure 63 Pressure buildup with flow in ASTM and Griffith Mk2 cells](image)

All the curves followed the expected parabolic pressure-flow relationship \((r^2 = 0.9908\) to 0.9998 for a parabolic fit to the data). The pressure build-up with flow in the Griffith Mk2 cell was very small, even at high flow rates. At 500 mL min\(^{-1}\) the pressure build-up due to the cell alone was less than 5 Pa and with the GloveTest rig it was still only 8 Pa. However, the pressure drop of the cells in the GloveTest rig was a more realistic test of cell performance. There would be little gain in reducing the plumbing for the PID and temperature sensor downstream of the GloveTest rig.

The pressure imbalance with collecting flow rate for both the cells can be largely attributed to the GloveTest rig downstream of the cells, not to the cells themselves. Despite the smaller size of the Griffith Mk2 cell, the pressure imbalance was less than
that in the ASTM cell. When the same normalised flow rates were used in each cell, the pressure drop in the Griffith Mk2 cell was less than that in the ASTM cell.

5.4.4 Results of Sample Distension Experiment

The relationship between static pressure and distension of the centre of the neoprene sample is shown in Figure 64. The distension of the new sample in the ASTM cell shows a complex shape characteristic of the non-linear elasticity of rubber.

![Figure 64 Effect of static pressure on distension of neoprene sample](image)

The used neoprene sample in the ASTM cell was initially stiffer, but the curves for new and used became parallel indicating the same stiffness from 3000 to 12,000 Pa. The shape of the curve for the Griffith Mk2 cell was flatter and the distension less. The backpressure due to flow produced pressures of less than 700 Pa for all cells in Figure 63, so this operational range is shown in Figure 65.
5.4.5 Discussion of the Effect of Collecting Flow Rate on Pressure in Cells

The attachment of sensors, connecting lines and diverting poppet valves downstream of the cells and the length of the connecting lines were the major determinants of the pressure build-up in both the ASTM and Griffith Mk2 cells.

In the literature review, published pressure build-up with flow in ASTM cells was given. This data has been overlaid in Figure 66. The pressure scale has been changed to a log scale to enable the curves to be compared.
Perkins and Ridge's (1986a) ASTM cell with large stopcocks gave essentially the same pressure build-up as for the ASTM cell (with a 3 mm orifice in the stopcock) and the Griffith Mk2 cell, both in the GloveTest rig. There were few details of their experimental setup but it appears that his downstream flow impedance was similar to the GloveTest rig. Both ASTM cells used by Perkins and Ridge (1986a), and Anna et al. (1998) gave a much higher pressure build-up. The unusual shape of their curve on the logarithmic scale may be due to mechanical friction at low-pressure readings of the Magnehelic gauge that was used.

The pressure drop with the Griffith Mk2 cell should be compared with the pressure drop of other cells, with the collecting flow rate scaled to the exposed test sample area. As the limiting factor in the pressure build-up in the cells appeared to be the GloveTest rig, the greatest gains in limiting the pressure build-up in the cells was by using the lowest flow rate that would give a true measurement of permeation rate. As smaller cells require a lower flow rate to give the same permeant concentration in the effluent flow, all the Griffith cells have this advantage over the ASTM cell.

The lower limit on cell size is addressed in Chapter 6, where edge effects become important. Very low collecting flow rates also decrease the response time of a test system, as it takes longer to sweep the collecting volume of a cell and the downstream
plumbing. The analytic sensitivity is increased at low flow rates as the permeant is more concentrated, though the data may be erroneous (Anna et al., 1998).

At a flow of 10,000 mL minute for both cells in the GloveTest rig, the distension of the samples was small. The distension for the Griffith Mk2 cell was 0.4 mm and for the ASTM cell it was 1.4 mm. In normal operation the Griffith Mk2 cell (500 mL min\(^{-1}\)) would produce a back-pressure of 10 Pa and an estimated deflection of 2 \(\mu\)m, too small to measure. For the ASTM cell (2000 mL min\(^{-1}\)) the pressure was 50 Pa and the measured deflection at this pressure was 0.15 mm. The differences between the pressures in the ASTM cell for different collecting flow rates (Figure 58) make estimates of data different. The differences may be due to the size of the stopcocks in the ASTM cell and the plumbing downstream from the cell. The following table may be indicative of the differences in pressures between test systems at different flow rates.

**Table 13 Pressure differential in ASTM cells for different collecting flow rates**

<table>
<thead>
<tr>
<th>Flow Rate (mL min(^{-1}))</th>
<th>Anna et al. (1998), ASTM cell</th>
<th>ASTM cell in GloveTest rig</th>
<th>ASTM cell alone</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2142</td>
<td>60</td>
<td>3</td>
<td>ASTM minimum flow rate</td>
</tr>
<tr>
<td>150</td>
<td>2148</td>
<td>60</td>
<td>4</td>
<td>ASTM maximum flow rate</td>
</tr>
<tr>
<td>500</td>
<td>2196</td>
<td>62</td>
<td>5</td>
<td>Anna et al. (1998) - suggested rate</td>
</tr>
<tr>
<td>2000</td>
<td>2855</td>
<td>90</td>
<td>11</td>
<td>This work, with ASTM cell</td>
</tr>
</tbody>
</table>

For the ASTM cell modified by Perkins, the same flow-pressure results were obtained as the present ASTM cell and the distension would have been small. However, the very large pressures experienced by Anna et al. (1998) with similar soft rubbery polymers would have produced significant stretching and thinning of the samples and overestimates of the SSPR at high flow rates. An acceptable 1.4 mm distension would be expected at 4 L min\(^{-1}\), but at 10 L min\(^{-1}\) the distension would have been 8 mm and significant increases in permeation may be expected. Flow rates of 10 Lpm were used by Perkins and Ridge (1985) to match the ASTM cell to a Miran 1A analyser to permit an acceptably short response time. Boring the stopcocks to 8 mm reduced the pressure within the ASTM cell.

In practice, the tendency appears to be moving been towards the use of detectors that sample the flow rate from the permeation cell, rather than requiring a large (10 Lpm) flow rate through the cell for Miran infrared analysers. Under these conditions,
distension of the sample by the collecting flow may not be an issue. However, Anna et al. (1988) has shown that the recommended flows through the ASTM F739 cell may be inadequate to measure the true SSPR. The Griffith Mk2 cell overcomes any tendency for the sample to distend with pressure, as there is negligible pressure buildup, even at very high flow rates.

The data presented in this section indicates that the SSPR for acetone is close to the true SSPR at the flows measured and that over a wide range of flows the SSPR for acetone is independent of the collecting flow rate. However, there is a need to perform further experiments at lower flow rates with all the cells and with a range of solvents.

**SECTION 5.5 EFFECT OF DEPTH OF SOLVENT ON PERMEATION**

In the course of this research, many permeation trials were performed using acetone and reference neoprene. The amount of solvent over the neoprene sample varied in each trial, but the Griffith cells and the Griffith Mk2 cells were usually filled with approximately 0.9 mL of solvent, the capacity of a Pasteur pipette. It was unusual for the sample to be dry at the end of even a long trial, as extra acetone was added at intervals. The amount of acetone appeared to make no real difference, but the effect of solvent depth to distend the sample, had not been specifically investigated.

The body of the Griffith Mk2 cell produced an exposed area of 3.14 cm² and Table 14 translates solvent volume to depth and pressure imbalance. The figures for the Griffith cell are similar.

<table>
<thead>
<tr>
<th>Solvent volume (mL)</th>
<th>Solvent depth (cm)</th>
<th>Pressure (acetone, Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.32</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.64</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>0.95</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>1.59</td>
<td>123</td>
</tr>
</tbody>
</table>

Figure 67 shows the permeation curves for different depths of solvent. All the curves show the same characteristic shape. Griffith Mk2 cell validation study data from Table 11 have been overlaid in Figure 67. The Griffith Mk2 SSPR mean has been used to scale this data. The scatter of the data is much better than acceptable using the ASTM criterion, but not as good as for the very precise data for the very careful Griffith Mk2 validation studies.
Figure 67 Effect of solvent depth on permeation, Griffith Mk2 cell, acetone vs reference neoprene

There was no trend suggesting that solvent depth affects permeation either in BT or SSPR. This suggests that any effect of solvent depth was less than the variability associated with the permeation measurements. Williams (1979) found that solvent depth did not affect BT, but said nothing about the effect on permeation rate. Anna et al. (1998) noted that an increase in the pressure differential should decrease the sample thickness and increase the surface area and thus increase the permeation rate. There appears to be no published data showing an increase in permeation rate with increased pressure differential on a clamped CPC test sample.

The depth of solvent could be expected to be an issue with mixtures, if components of the mixture permeate at different rates, leading to different concentrations on the exposed side. A smaller volume or depth would increase the effect with mixtures, as it would provide a smaller reservoir. However, a larger reservoir in itself may have little effect unless there is mechanical mixing of the challenge chemical as stratification could occur.

SECTION 5.6  EFFECT OF THICKNESS MEASUREMENTS ON INTERPRETATION OF DATA

The previous sections addressed factors that could affect the permeation rate. The following sections address the factors that affect the interpretation of permeation data.
This section addresses the measurement of sample thickness. In comparing permeation data from different samples, the SSPR should be inversely proportional to the sample thickness and the BT approximately inversely proportional to the square of the thickness, over a small range of thicknesses.

A dial gauge (Mitutoyo 2109F, 1 μm readability, 3 μm stated accuracy) on a heavy stand with a flat, stainless steel anvil was used to measure thickness. The standard foot on the dial gauge was rounded and would have led to a very small contact area between the foot and specimen and an obvious indentation. It was replaced by a 5-mm diameter flat circular foot, to minimise indentation of the specimen.

As the dial gauge was spring loaded, there was some concern that the thickness of the specimen could alter the clamping force. In addition, the method of placing the dial gauge on the specimen could affect the precision of the measurement.

Trials of thickness of the supported glove samples cut with a wad punch had showed a poor correlation between sample thickness and sample weight (Bromwich et al., 1997). Methods of correlating sample weight with thickness would be useful, particularly for supported samples where the thickness would be difficult to determine precisely. There was a tendency for test samples to curl, and a vacuum plate was developed to hold the sample flat during thickness measurements.

5.6.1 Thickness Experiments
Four experiments were designed to investigate different aspects of thickness measurements mentioned above.

**Experiment 1. Dial gauge indentation in test sample**
The indentation of the sample due to the preloading of the dial gauge was determined by first measuring the clamping force exerted by the dial gauge stem for different dial gauge readings. This clamping force was then related to the indentation of the sample by the dial gauge with different loadings on the dial gauge stem. Direct measurement was not possible, as the neoprene was somewhat stiffer than the balance.

The dial gauge was positioned with a magnetic dial gauge stand (Fuji) on a precision steel measuring table above a top pan balance (Mettler PM1200, 1200 g, 1 mg readability) as shown in Figure 68. The balance was placed on a laboratory jack that
was also on the measuring table. The balance was levelled with its own level gauge and checked at intervals.

![Dial gauge, balance, laboratory jack and measuring table](image)

Figure 68 Dial gauge, balance, laboratory jack and measuring table

The balance was then raised to contact with the foot of the dial gauge and then further to deflect the dial gauge over its 1-mm range in 100 μm stages. The laboratory jack was quite stiff and difficult to raise a precise, small amount, but on lowering the balance from the dial gauge, both instruments returned to zero. This ability of the dial gauge to return to zero demonstrated that the dial gauge spring prevented hysteresis.

The second part of this experiment measured the indentation of the dial gauge with additional loads on the dial gauge stem, effectively measuring the elasticity of the sample. Hooke's law for the extension of a spring may be stated in terms of the relationship between the compression of the neoprene \( X \), the constant of elasticity \( k \) and the weight \( W \) (or force) needed to produce compression for a given foot.  

\[ kX = kW \]

........................................ Equations 11 Hooke's Law

The stem of the dial gauge was loaded with solid cylinders of metal and the thickness of the reference neoprene was recorded with this increased load. The first weight acted as a platform for successive weights and had a blind hole drilled in it to fit on the stem of the dial gauge that protruded through the top of the gauge. The weight-deflection curve gave the elasticity \( k \) of the neoprene to predict the deflection for a given clamping weight with a 5 mm diameter foot. The stem of the dial gauge was loaded with weights up to 500 g. This was well in excess of the clamping pressure that would be produced by most dial gauges, but may be similar to than that produced by some screw micrometers.
A simple scaling of the neoprene elasticity for dial gauge feet of different areas would not be expected, as the neoprene surrounding the foot would be under tension and relate more to the circumference of the foot, whereas the area under the foot would be in compression and relate to the area of the foot. This conjecture was not tested.

**Experiment 2. Effect of dial gauge placement technique**

The technique of placement of the dial gauge foot on the test sample was a potential source of error in estimating sample thickness. If the dial gauge stem was released before the foot contacted the test sample, then the slight friction of the dial gauge mechanism would leave the foot more embedded in the test sample. For the experiment, the dial gauge foot was placed directly on the balance pan a number of times at different deflections of the dial gauge produced by jacking the balance. The foot was released at distances between contact with the balance pan and about 0.1 mm above the balance pan. The dial gauge readings and corresponding static forces on the balance were recorded.

Direct measures on the neoprene sample were not possible because the neoprene was much stiffer than the balance mechanism. However, with knowledge of the elasticity of the balance and the elasticity of the neoprene, the balance pan data could be scaled to estimate the degree of embedding of the gauge foot in the neoprene when the dial gauge stem was released.

**Experiment 3. Sample thickness and sample weight**

For unsupported CPC polymer membranes of uniform density, an extrapolated relationship between sample weight and sample thickness was expected to show zero weight at zero thickness. This assumed the punching of the samples produced samples of the same diameter and uniform density of the neoprene.

Eight sequential 25 mm diameter samples were prepared with a wad punch from a strip of reference neoprene and weighed on a Sartorius M5 microbalance (5 g ± 1 μg). Trials with a wooden board showed that small splinters from the board became embedded in the sample, making a significant difference to the weight, so a polypropylene breadboard was used with the wad punch. Five measurements of thickness were made, over the surface of the samples, including one in the middle of the sample.
With a uniform density, \( \rho \), and constant area, \( A \), the weight, \( W \) and thickness, \( L \) are linearly related

\[
W = L \rho
\]

Equation 12 Sample weight

Trials with digital callipers (readability .01 mm) and a large magnifying glass indicated that the diameter could be reliably estimated to within 0.1 mm. The roundness of punched samples was found to vary by 0.2 mm. A 0.1 mm variation in diameter of the samples could account for 1.4% variation in the weight of the samples.

**Experiment 4. Vacuum plate**

The ASTM F739-1996 requires thickness to be measured to within ±20 \( \mu \)m but the gauge was readable to 1 \( \mu \)m. It was not known whether holding the sample flat in a replicable manner with a vacuum plate would produce better estimates of sample thickness.

A vacuum plate was developed to fit over the anvil of the thickness gauge as shown in Figure 69.

![Figure 69 Vacuum plate](image)

The test sample "A" was placed on a sintered glass plate "B". The plate was supported by a PVC ring that was sealed to the dial gauge anvil by an O-ring. A vacuum line provided a negative pressure to the sintered glass plate, holding the sample flat. To minimise bowing of the glass plate under vacuum, a support peg was placed between the sintered glass plate and the anvil of the gauge. A polythene film (invisible in the photograph) with a hole in the centre permitted contact of the gauge foot with the sample but sealed the visible part of the sintered glass plate, ensuring a better vacuum.
For the experiment, a vacuum was applied to the vacuum plate, and then slowly reduced. A vacuum gauge monitored the vacuum line. If the vacuum plate was to be of use, changes in the vacuum would have little effect on the deflection of the sintered glass plate.

### 5.6.2 Results of Thickness Experiments

**Results of Experiment 1. Dial gauge indentation in test sample**

Figure 70 shows the effect of raising the jack and recording the dial gauge reading and balance reading as the laboratory jack was raised. This was done in the absence of a sample and gives the elasticity of the dial gauge spring.

![Figure 70 Clamping force of dial gauge with dial deflection](image)

The force on the balance produced by the dial gauge was about 100 g for a deflection of 400 μm, the thickness of the reference neoprene. The results of second part of this experiment are shown in Figure 71, with a linear relationship between the load and the compression of the neoprene, a classic Hooke’s law curve.
Figure 71 Elasticity of neoprene

The linearity of the data in Figure 71 indicates that the elastic limit of the neoprene was not reached. From a least squares fit to the data, the data in Table 15 was calculated. The minimum and maximum clamping force values are taken from Figure 70.

Table 15 Depression in ASTM neoprene by Mitutoyo 2109F dial gauge

<table>
<thead>
<tr>
<th>Clamping Force (g)</th>
<th>Depression in reference neoprene (μm)</th>
<th>Standard Deviation (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>70</td>
<td>1.6</td>
</tr>
<tr>
<td>Average</td>
<td>100</td>
<td>2.3</td>
</tr>
<tr>
<td>Maximum</td>
<td>120</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The correction of +2.3±0.7 μm to measurements of the thickness of reference neoprene to account for the 100 gram clamping force of the dial gauge is much smaller than the required ±20 μm tolerance recommended by ASTM F739-1996.

Results of Experiment 2. Effect of dial gauge placement technique

Figure 72 shows a plot of the clamping force adjusted at intervals of about 200 g and the stem released with the foot in contact up to 0.1 mm above the balance pan. The least squares best-fit line from Figure 70 is overlaid on this plot as a dashed line. Excursions below this line are due to the placement of the dial gauge foot. The lower, dotted line in Figure 72 typifies a balance reading with the dial gauge foot released about 0.1 mm from the balance pan.
The gauge had some mechanical resistance and the manner in which the shaft was lowered was difficult to replicate. The balance was deflected by the spring in the dial indicator, showing a similar curve to the Figure 70, but with greater scatter. For the 400 μm thickness of reference neoprene, a clamping force of 100 g could be expected, if the dial gauge was released almost touching the sample.

Differences in measured neoprene thickness up to 10 μm were found with repeated placements on the same spot, if the sample was moved. Some of this was due to the build-up of debris on the foot of the dial gauge, as the dial gauge did not return to zero on removal of the sample. The rest was due to placement of the foot of the dial gauge. Figure 73 shows the deflections of the neoprene and Mettler balance with weights, and the balance with placement of the foot, up to 0.1 mm from the balance.
The neoprene was 18 times (42/2.4) stiffer than the balance mechanism. A 60 μm deflection of the balance, corresponding to a 0.1 mm drop of the dial gauge foot, would be expected to embed only 3.3 μm (60/18) in the neoprene. With careful placement of the dial gauge, this could be reduced to about 1 μm or less.

**Results of Experiment 3. Sample thickness and sample weight**

All clamping forces have been expressed in terms of the balance weight rather than the more technically correct units of Newtons (grams x 9.8).

The error bars in Figure 74 for the eight samples represent one standard deviation in the thickness measurements for each sample of reference neoprene.
Both sample weight and sample thickness show the same trend from sample one to sample eight taken from along the sample, revealing variations attributable to manufacture. The variation in thickness of each sample was less than variations along the sheet of reference neoprene. However, a least squares regression of sample weight against sample thickness does not show that zero sample thickness would give zero sample weight (Figure 75), though the extrapolation of the data at the most suggests that a simple proportionality between weight and thickness does not exist. A 10% increase in thickness does not result in a 10% increase in weight.
Figure 75 Sample weight and sample thickness

The standard error (SD/mean) of the pooled sample weights is 0.7% but 2.3% for the pooled thickness data, suggesting greater variability of the thickness than the sample weight. The magnified digital callipers could account for 1.4% of the variation in sample area by variations in sample diameter, so area estimates were less sensitive than weight in discriminating variations in sample size.

Results of Experiment 4. Vacuum plate

As the vacuum on the vacuum plate was reduced, the dial gauge indicated some deflection of the vacuum plate.
Reducing the vacuum to a 50% vacuum from 100% vacuum produced a deflection of the vacuum plate of 5 μm, but releasing the vacuum to atmosphere produced a further 17 μm deletion.

5.6.3 Discussion of Thickness Experiments

ASTM 739 (1996) requires a determination of the thickness to be within 20 μm. The bias produced by the clamping of the dial gauge was much less than this and a correction of +2.3±0.7 μm could be applied for reference neoprene. There was a further underestimation of the neoprene thickness of up to 1 μm produced by the tendency of the dial gauge foot to embed in the neoprene when the dial gauge stem was released very close (<0.1 mm) to the neoprene. The elasticity of other CPC polymers would be expected to be similar or more than that of neoprene and so the finding may be generally applicable.

The steady state permeation \( P \) was previously given as the product of \( D \) (cm\(^2\) min\(^{-1}\)) and solubility \( S \) (g g\(^{-1}\)) per unit thickness \( l \).

\[
P = \frac{D S}{l} \text{ (μg cm}^2\text{ min}^{-1})
\]

................................. Equation 13 Permeability

and The Lag Time \( LT \) was given as
If the reference neoprene varied in thickness by up to 20 μm, the precision allowed in ASTM F739-1996, and the material was nominally 400 μm thick, then the acceptable estimates of thickness would be between 380 and 420 μm. This uncertainty in thickness produces an uncertainty of ±10% in LT and (to a reasonable approximation) ±10% in BT and ±5% in SSPR. For procedures to determine thickness to be comparable there is a need to estimate factors that could contribute to variations in the estimates of thickness.

The 2.3±0.7 μm depression caused by the dial gauge clamping force underestimated the thickness and produced a BT and LT about 1%±0.3% greater than expected and a SSPR 0.5%±0.2% less than expected. These differences were not experimentally significant.

For other dial gauges with a 5 mm circular foot, the relationship between the clamping force at 400 μm, and depression of the reference neoprene is

\[
\text{Depression (μm)} = \text{Clamping force}_{400 \text{ μm}} (g) \div 42
\]

If the requirements for thickness measurements were to be tightened to reduce the uncertainty attributable to thickness, then there are obvious limits (using reference neoprene), of 2 μm to the accuracy of the technique and limits of 0.7 μm to the precision of the technique. To this has to be added the uncertainty of the additional embedding of the dial gauge foot on release of the foot of 1 μm.

A loose relationship between sample weight and sample thickness was found, with 66% of the variation in sample thickness explained by variations in sample weight. Density variations may have occurred and thinner samples had a higher density. This may occur during manufacture when milled neoprene is compressed between rollers and the spacing of the rollers varies. As mentioned in “Results of Experiment 3. Sample thickness and sample weight” on page 1, magnified calliper measurements of the diameter of the samples could account for 1.4% of the variation in the sample area.

The vacuum plate has the potential to improve the measurement of thickness of samples, particularly if they do not lie flat. A 10% loss of vacuum (10 kPa) would result...
in a 1 μm decrease in the estimation of the sample thickness, through deflection of sintered glass plate.

Overall, efforts to develop better measurements of thickness are of limited value, as a comparison of similar materials of different thicknesses requires that the density of the materials be the same.

SECTION 5.7 EFFECT OF SAMPLE PREPARATION ON PERMEATION DATA

On addition of the acetone to the Griffith cell during the cell validation experiments, there was an hitherto unobserved, immediate fast response of the detector, peaking at about one minute, followed by an exponential decay of at least eight minutes.

If the source of this immediate response was an emission from the test sample, then a reduction of the magnitude of this response could be expected with removal of some of the unidentified contaminant from the sample. Ehntholt et al. (1990) had used silicon rubber as a collecting media, so it was reasonable to suppose that the reference neoprene had acted as a passive absorber of atmospheric contaminants or that there were residual contaminants in the material from manufacture.

5.7.1 Trials with Sample Preparation

**Effect of vacuum heating the sample on background emissions**

Samples were heated in a vacuum oven at 60°C for 15 minutes in order to remove volatile contaminants. A temperature of 60°C was chosen, as much higher temperatures have been known to change the character of CPC during decontamination (Perkins, 1991). Washing of the sample with a solvent would only compound the problem.

![Electric frypan vacuum oven with polycarbonate lid](image)

**Figure 77 Electric frypan vacuum oven with polycarbonate lid**

Results from the Griffith cell validation trials for treated and untreated samples are shown in Figure 78 (same as Figure 38). The permeation curves are plotted on a logarithmic scale to emphasise the noise in the signal before breakthrough was detected.
The ASTM F739 (1996) inter-laboratory acceptance limits are used in Figure 78 as an absolute metric rather than the inter-laboratory acceptance limits. They have a similar precision to the that obtained with this data for the Griffith cell (Table 11).

![Figure 78. Breakthrough time and ASTM inter-laboratory acceptance limits](image)

The nature of the diffusion process is such that a near immediate but undetectable breakthrough is predicted. The “zero” permeation rate just prior to the addition of the acetone was set to a slightly positive value of 0.003 μg cm\(^{-2}\) min\(^{-1}\) rather than straddling zero, to allow the data to be shown on a logarithmic scale. This small offset had no significant effect on the determination of either the nBT or the SSPR.

The immediate detection of an unknown volatile chemical from the samples was much less evident in the pre-treated neoprene samples. The signal from the untreated samples did not quite return to the pre-test levels before breakthrough.

A second trial was performed to estimate weight loss of the reference neoprene samples during this vacuum heating. Seven samples for various cells were vacuum heated at 60°C for 30 minutes. The weight loss averaged 0.35% in each sample, see Table 16. The loss is also expressed as an average weight loss in μg cm\(^{-2}\).
Table 16 Sample weight loss with vacuum heating at 60°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (mm)</th>
<th>Pre treatment (mg)</th>
<th>Post treatment (mg)*</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>60</td>
<td>1808.290</td>
<td>1801.8</td>
<td>0.36%</td>
</tr>
<tr>
<td>Griffith</td>
<td>26</td>
<td>348.224</td>
<td>347.1</td>
<td>0.32%</td>
</tr>
<tr>
<td>Griffith</td>
<td>26</td>
<td>336.688</td>
<td>335.52</td>
<td>0.35%</td>
</tr>
<tr>
<td>Griffith Mk2</td>
<td>25</td>
<td>303.097</td>
<td>302.034</td>
<td>0.35%</td>
</tr>
<tr>
<td>Griffith Mk2</td>
<td>25</td>
<td>310.900</td>
<td>309.957</td>
<td>0.30%</td>
</tr>
<tr>
<td>Griffith Small</td>
<td>14</td>
<td>100.220</td>
<td>99.902</td>
<td>0.32%</td>
</tr>
<tr>
<td>Griffith Small</td>
<td>14</td>
<td>101.517</td>
<td>101.055</td>
<td>0.46%</td>
</tr>
</tbody>
</table>

Average weight loss: 0.35%±0.05%, 225 μg cm⁻²

* Post treatment weights are given to a stable digit on the microbalance as the weight slowly increased on removal from the vacuum oven.

During weighing, the sample weight slowly increased, presumably due to water vapour or other material in the atmosphere being absorbed into the surface pores of the sample.

**Effect of clamping the sample on background emissions**

An experiment, incidental to the validation process, was performed to determine whether adjustments to the cell clamping bolt affected the background signal. This was done with a steady, low background prior to the addition of acetone. If neoprene is considered to be like a sponge, then squeezing it should release some residual volatiles from the polymer matrix.

It was expected that any effect from tightening the clamping bolt would be less than a total release of volatiles from the neoprene due to stresses caused by the addition of acetone. The direct squeezing effect would be limited to the material under and very near the clamped areas of the neoprene. However, it was observed that tightening the clamping bolt squeezed polymer from under the clamped region and bowed the sample slightly.

A part turn of the clamping bolt gave the curve in Figure 79, extracted from Trial D in Figure 214. The initial sharp peak caused by the tightening of the clamping bolt is followed by the peak from the addition of acetone. It demonstrates the importance of constant experimental conditions in obtaining a low noise background.
The peak from turning the clamping bolt rises and falls more quickly than that from the addition of acetone.

Figure 79 Effect of squeezing sample
5.7.2 Discussion of Sample Treatment Trials

In the first six minutes, the emission from the untreated samples in Figure 78 was calculated by trapezoidal integration to be 0.04 μg cm\(^{-2}\). If this was compared with the weighed loss of 225 μg cm\(^{-2}\) from Table 16, then the measured emissions only accounts for 0.036% of the weight loss, if 0.04/225 = 0.018% was lost from each surface of the sample during vacuum heating at 60°C. This assumes that the PID (with an ionisation potential of 10.8 eV) was a reliable indicator of these emissions and that emissions detected have a similar analytic sensitivity as acetone. As volatile organic compounds tend to be small and these tend to be detected, it is likely that emissions would be detected by the PID.

Though water vapour is not directly detected by this PID, high humidity readings will case the reading to dip below zero or slowly climb (EPA, 1994). This was not the behaviour observed, but an experiment with a step change in the humidity of the nitrogen would indicate whether the peak could, at least in part, be attributed to water vapour from the sample.

Overall, the small percentage detected (0.018%) suggests that only a small amount of organic vapour was released and that emission was from close to the "inside" surface of the sample. Vapours undetectable by PID, such as water vapour, were probably released in greater amounts. Other analysis such as GC analysis would be required to identify the emissions.

A possible mechanism for the immediate response of the PID on the addition of the acetone was that the acetone almost immediately sets up stresses in the exposed surface of the neoprene sample. These stresses may produce a slight stretching of the sample, releasing some absorbed air contaminants or other volatile material present on the opposite surface of the sample. Perkins et al. (1987a) noticed "ghost" GC peaks on decontamination of butyl gloves from breakdown of the polymer matrix at 100 °C, but this was related to the treatment of the polymer rather than the addition of a test chemical. Davis et al. (1986) observed a similar effect, but not a peak, and left their test sample in a test cell for 1½ hours before measurement to "allow for vaporization of volatile compounds from the glove specimens and, thus, to establish a steady FID response baseline." Other researchers have used prolonged pre-test periods to reduce

Chapter 5. Effects of Operational Parameters on Permeation 148
background levels (Williams, 1979), but none reported a peak after the addition of the test chemical.

If there were significant releases of chemical from a CPC matrix or near the surface of the CPC immediately after exposure, then this has obvious implications for determining detection limits during permeation testing, and the method of determining detection limits. The treated samples gave a baseline that returned to near the analytic detection limit before permeation was evident, but the untreated sample remained above the background.

The squeezing action of the clamping bolt in Figure 79 supports the release of chemicals from the neoprene rather than some unknown source. The action of tightening the clamping bolt appears to be akin to squeezing a sponge, with a rapid release of material from the sponge and then a fast return to background levels. The time scale associated with this peak was much shorter than that from the addition of the acetone, indicating the mechanism associated with the addition of acetone was more diffuse.

In Appendix A of ASTM F739-1996 an approach to determine the minimum detectable permeation rate requires chemical to be injected into a cell with an aluminium sample in place of the test sample. This would produce an artificially low estimate of the minimum detectable permeation rate, as emissions from the sample are not present. To properly estimate the background permeation rate of a system, the whole system should be present, including the sample. This rate may be expected to vary with sample preparation, sample type, collection flow rate, and type and sensitivity of the detector.

The immediate release of chemical on the inside surface of an item of CPC on chemical exposure to the outside may also have implications for reuse of CPC that has been used with toxic chemicals. Small amounts of toxic chemical near the inside surface may be released on re-exposure of the outside to another chemical, despite apparent decontamination after use. Similar small releases may result from mechanical stresses set up by tasks.

SECTION 5.8   CONCLUSIONS

The conclusions in this chapter have been grouped to correspond to factors that affect permeation data and factors that affect the interpretation of permeation data.
5.8.1 Limitation of Tests

Only the acetone-reference neoprene concentration was tested and this may limit the applicability of the results. Further tests are needed to determine whether the permeation related findings are generally applicable, particularly as acetone is a volatile solvent. These further tests may show a decisive advantage of the Griffith cells over the ASTM F739 cell when low volatility solvents are used due to the high flow velocity next to the test sample. This view is based on the demonstrated need for a higher-than-recommended (500 vs 150 mL min\(^{-1}\)) collecting flow rate in the ASTM cell for many solvents (Anna et al., 1998).

5.8.2 Factors Affecting Permeation

**Flow patterns in cells**

The flow patterns in the three cells are described as follows:

- **Griffith cell.** Acceptable. Asymmetric but without stagnation.
- **Griffith Mk2 cell.** Excellent. Radially symmetric, with no possibility of stagnation.
- **ASTM cell.** Generally acceptable, but with significant areas of stagnation away from the test sample. The depth of the cell prevented valid observations of the flow pattern next to the sample.
- There is scope for additional quantitative studies of cell clearance by measuring the concentration of a dye or tracer gas in the effluent flow and the development of other methods to reveal regions of poor flow next to the test sample.

**Effect of collecting flow rates on permeation**

- The permeation rate for acetone-reference neoprene is not significantly affected by the flow rate through the Griffith cells over a large range of flow rates.
- At low flow rates, the permeation rate is underestimated in the Griffith Small cell, but estimates of the acceptable range for acetone and neoprene were not obtained due to the range of the PID.
- More elaborate experiments with less sensitive detectors or diluted flows to the PID would be required to detail the lower flow limit for use with the Griffith cells. However, the faster response of the Griffith cells make them perform at least as well as the ASTM cell at comparable normalised collection flow rates.
- The PID detector response is not affected by the collecting flow rate.
**Effect of collecting flow rate on pressure in cells**

- If collecting flows scaled for exposed sample area were used, then the pressure build-up in the cell may be greatly reduced by the use of small cells. The pressure drop in associated plumbing downstream of the cell was the dominating factor.
- The pressure build-up with flow in the ASTM cell itself was dominated by small stopcocks and port sizes on the cell.
- If these stopcocks were enlarged, the limiting factor becomes the downstream attachments, particularly the length of plumbing and diverting valves. Keeping plumbing short and valves large minimises the pressure build-up.
- The distension of the reference neoprene from pressure build-up in the ASTM and Griffith Mk2 cells was negligible under normal operating conditions.

**Effect of depth of solvent on permeation**

- Solvent depth in itself was not an issue with single solvents, as long as the sample was wet. With a much greater solvent depth, and a thin sample, there may be sufficient thinning and enlargement to affect both the LT (and BT) and SSPR.

**5.8.3 Factors Affecting Interpretation of Permeation Data**

**Thickness experiments**

- The dial gauge underestimates the thickness of reference neoprene by 2.3±0.7 μm, giving BT and LT estimates 1%±0.3% greater than expected and a SSPR 0.5%±0.2% less than expected. However, this error is much less than the ±20 μm required by ASTM F739-1996.
- Careful placement of the dial gauge was required to minimise the tendency of the foot to embed itself in the test sample. Good technique could reduce this to 1.5 μm or less.
- Sample weight correlates poorly with sample thickness, with only 66% of thickness variations being explained by weight variations. It is likely that the density of the neoprene varies, with thinner samples of the neoprene being denser. This limits application of improvements in estimates of sample thickness.
- A vacuum plate can hold samples flat to facilitate thickness measurements, but a 10 kPa reduction (1/10 atmosphere) in the vacuum would decrease the estimate of the sample thickness by one micron due to deflections of the sintered glass plate.
**Sample preparation**

- Sample preparation may be required to remove residual chemicals in the matrix of CPC samples to permit the determination of the minimum detectable permeation rate.

- The ASTM F739-1996 "Appendix A" method for estimating detection limits permits an optimistic estimate of the minimum detectable permeation rate by the use of an aluminium sample in place of a CPC sample as it was found that the sample itself may produce low level emissions.

- An understanding of induced emissions from the CPC may have some application in the workplace, though the effect may be minute. If the matrix of an item of CPC was contaminated with a very toxic chemical, then there may be an immediate, low level release of the chemical inside the CPC, with the mechanical stresses of use, or exposure to another chemical.
CHAPTER 6. MODELLING CONTINUOUS EXPOSURE

SECTION 6.1 AIM

This chapter implements mathematical models to further explore theoretical aspects of permeation through CPC. Mathematical models of permeation are important as they give credence to explanations of experimental data and permit predictions of behaviour outside what has been measured. Where a model does not fit the experimental data, modifying the model may improve its predictive value.

Simple analytic solutions to a permeation model based on Fick's Second Law will be used to

- examine the effect of analytic detection limits on breakthrough time (BT) and Lag Time (LT);
- discover how well estimates of diffusivity (D) and solubility (S) from the permeation experiments can be used to model the experimental permeation curves; and
- provide a reference point for numeric solutions of the model for intermittent exposure, as continuous exposure is a special case of intermittent exposure.

SECTION 6.2 INTRODUCTION

Relatively little has been published in the industrial hygiene literature on modelling of permeation through CPC. The indices most commonly used in describing the performance of CPC are BT, BDT, nBT, LT and SSPR. Of these, LT is loosely based on the presumed simple diffusion of a chemical through an item of CPC with a constant diffusion coefficient "D". By generating permeation and permeation rate data with the analytic solutions, the theoretical performance of BT and LT with different analytic detection limits could be investigated. During the implementation of the analytic solutions, trials were performed to determine the analytic limitations of the solutions and to replicate published data.

In this chapter, D is assumed to be constant, and not vary with concentration or time. Temperature is constant. Analytic solutions were chosen and solved using a series solution of Fick's diffusion equation, derived from Crank’s text "The Mathematics of Diffusion" (1975). In Chapter 10, a numerical solution with concentration dependent diffusion is developed.
SECTION 6.3 STANDARD CONDITIONS

Two approaches could have been taken to establishing a set of reference conditions to provide realistic values for the analytic solutions to Fick's Second Law.

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

................................. Equation 15 Fick's Second Law

The boundary conditions for a membrane of thickness L that is initially dry and kept with a zero chemical concentration on the collecting surface are:

Initial, \( t = 0 \), \( C(x, 0) = 0 \)

Time \( T \), \( t = T \), \( C(0, T) = C \), \( C(L, t) = 0 \)

One approach would have been to implement a solution with the time, permeation and permeation rate scales dimensionless, and then scale any experimental data to fit the solution. This may have made the solution universal, but it would only be applicable to the workplace if the fit between the solution and data was good, as non-linearities would be difficult to scale appropriately. The second approach was chosen, adjusting the solution to fit the experimental data. This would then show where the solution failed to adequately describe the experimental data.

The "Standard Conditions" in Table 17 were established and used for the solution. The conditions used by Schwope et al. (1988) for modelling glove permeation gave reference points for comparing calculated data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPC Thickness</td>
<td>0.05 cm</td>
<td>Used by Schwope et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>0.04 cm</td>
<td>Reference neoprene from ASTM F739 (1996)</td>
</tr>
<tr>
<td>Dry Concentration</td>
<td>0 µg cm(^{-3})</td>
<td>Assumed instant removal of permeant</td>
</tr>
<tr>
<td>Wet Concentration</td>
<td>10,000 µg cm(^{-3})</td>
<td>Any large number would suffice. Used where comparison with the data of Schwope et al. was not an issue.</td>
</tr>
<tr>
<td>Solubility</td>
<td>4.9.10(^4) µg cm(^{-3})</td>
<td>Used by Schwope et al. (1988)</td>
</tr>
<tr>
<td>Initial Concentration</td>
<td>0 µg cm(^{-3})</td>
<td>Assumed no chemical in CPC matrix at start</td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
<td>2.5 10(^{-6}) cm(^2)min(^{-1})</td>
<td>Used by Schwope et al. (1988)</td>
</tr>
</tbody>
</table>

SSPR is said to exist after a period of three Lag Times (Crank, 1975), as the plotting of graphs can not visually distinguish between permeation rates after this time. A time of six Lag Times was used to ensure steady state conditions were established for half the experiment time.
SECTION 6.4 IMPLEMENTATION OF ANALYTIC PERMEATION SOLUTION

Solutions for Permeation Rate and Cumulative Permeation are presented which were then coded for use in a computer spreadsheet.

6.4.1 Permeation Rate (PR)

Crank's (1975) series solution of Fick's First Law for permeation rate is

\[
Flux = \frac{SD}{l} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-\frac{4\pi^2 Dn^2t}{l^2}} \right\}.
\]

...............Equation 16 Solution to Fick's second law

where

- \( Flux \) flux or permeation rate per unit area (μg cm\(^{-2}\)min\(^{-1}\))
- \( S \) solubility (μg cm\(^{-3}\))
- \( D \) diffusion coefficient (cm\(^{2}\)min\(^{-1}\))
- \( l \) thickness of membrane (cm)
- \( t \) exposure time (min)

The permeation rate through the membrane is inversely dependent on the thickness \( l \) and since the summation term converges, the steady state permeation rate \( P \) is proportional to the product of the solubility \( S \) and diffusion coefficient \( D \).

\[
P = D \frac{S}{l}
\]

.................................Equation 17 Permeability

Using Equation 16, the permeation rate curve was calculated for values of \( D = 2.5 \times 10^{-6} \) cm\(^{2}\)min\(^{-1}\), \( S = 4.9 \times 10^4 \) g cm\(^{-3}\) and \( l = 0.05 \) cm, as shown in Figure 80.
By either integrating the permeation rate (which tends to accumulate errors) or directly calculating the cumulative permeation, the amount of chemical permeating the membrane at a given time can be estimated.

### 6.4.2 Cumulative Permeation (CP)

Cumulative Permeation is the time integral of the permeation rate. Crank's text (Crank, 1975) also gives a solution to Fick's Second Law using a series expansion to give the Cumulative Permeation $Q_t$, directly, thus avoiding integration errors.

$$
Q_t = D(C_1 - C_2)\frac{l}{l} + \frac{2l}{\pi^2} \sum_{n=1}^{\infty} \frac{C_1 \cos(n\pi) - C_2}{n^2} \left(1 - e^{-D\frac{l^2}{n^2} t}\right) + \\
\frac{4C_0 l}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m+1)^2} \left(1 - e^{-D\frac{l^2}{(2m+1)^2} t}\right)
$$

$\cdots\cdots\cdots$ Equation 18 Cumulative Permeation

where

- $Q_t$ cumulative permeation per unit area (μg cm$^{-2}$)
- $D$ diffusion coefficient (cm$^2$ min$^{-1}$)
- $C_0$ initial uniform chemical concentration within the membrane (μg cm$^{-3}$)
- $C_1$ chemical concentration at the outside surface of membrane (μg cm$^{-3}$)
- $C_2$ chemical concentration at inside surface of membrane (μg cm$^{-3}$)
- $l$ thickness of membrane (cm)
- $t$ exposure time (min)
If the chemical concentration inside the membrane $C_0$ is zero and the concentration $C_2$ "inside" the CPC is kept at zero, then the cumulative permeation curve asymptotes (Crank, 1975) to the line.

$$Q_t = DC_1 \left( t - \frac{i^2}{6D} \right)$$

... Equation 19 Cumulative permeation asymptote

This line intercepts the time axis at $\frac{i^2}{6D}$, the Lag Time.

### 6.4.3 Coding the Solutions to the Model

The computer code to express these solutions was written in Visual Basic for Applications (VBA) using double precision arithmetic and run within Excel'97 (see Appendix C for the code and details of its testing). Sufficient computational accuracy was obtained with 100 terms (Figure 81), particularly for small times (<7 minutes). Rounding errors associated with the computational engine in Excel were found to be acceptable. Separate code was written for the permeation rate and cumulative permeation to avoid cumulative errors associated with numerical integration of the permeation rate data.

Figure 81 shows the effect of number of terms on the permeation rate (Flux) calculation for the first 45 minutes with Standard Conditions and a sample thickness of 400 μm. The nBT permeation rate of 0.1 μg cm$^{-2}$min$^{-1}$ and corresponding nBT are also shown.
An increased number of terms is needed to accurately calculate the curves in the first few minutes, but even with 1000 terms, the model fails to produce a low initial permeation rate due to the computational limits of the Excel program and the microprocessor. Tests to demonstrate these limits are given in Table 35 in Appendix F. In practice, the calculation of the minute initial permeation rates (i.e. < 10\(^{-15}\) \(\mu\)g/cm\(^2\)/min) has little practical importance.

It was possible to calculate the BT for a given analytic detection limits or a set permeation rate, as shown in Figure 81. For these conditions, Excel's Solver function gave a 31.7 minute nBT at 0.1 \(\mu\)g cm\(^{-2}\)min\(^{-1}\) with less than a minute's iterations (Dell Pentium 133).

**SECTION 6.5 VALIDATION OF ANALYTIC SOLUTIONS TO MODEL**

Before the variants of the solution were applied, checks were performed to ensure that the calculated values were similar to Crank's data, as no instances could be found of the solution being implemented with the stated use of spreadsheets (Appendix G). The approaches used may have had a different precision or approach of calculation, so exact concurrence was not expected. Checks were performed using the PR and CP analytic solutions to ensure they gave the same figures as published BT and SSPR data.
6.5.1 Analytic Permeation Rate Solutions

Schwope *et al.* (1988) presented calculations of BT's for two thickness of CPC sample and two sample areas (Table 1 in Schwope *et al.*, 1988). These calculations were assumed to be valid and the calculations were repeated using the data of Schwope *et al.* (1988) and 100 terms with the Flux function to calculate PR's. The Solver routine in Excel was then used to iteratively calculate Breakthrough Times (BTs) for Permeation Rates (PR's) of 0.3 and 0.6 $\mu$g cm$^{-2}$min$^{-1}$ for the two sample areas. The calculated BT's and the percentage difference to the published data are shown in Table 18.

Table 18 Validation of BT calculations with the data from Schwope *et al.* (1988)

<table>
<thead>
<tr>
<th>Sample area (cm$^2$)</th>
<th>Thickness (cm)</th>
<th>Schwope <em>et al.</em> BT (min)</th>
<th>Calculated BT (min)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.05</td>
<td>70</td>
<td>70.48</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>14</td>
<td>14.40</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>368</td>
<td>367.46</td>
<td>-0.15</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
<td>92</td>
<td>91.86</td>
<td>-0.15</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>17</td>
<td>17.62</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>548</td>
<td>546.51</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

The calculated BT's for larger values agree if rounding errors are considered. Only one value differs by more than 3% (17 vs 17.62 minutes). This may be due to the rounding errors, different calculation of the figures, different mathematical precision, or number of terms. A publishing error in the data of Schwope *et al.* (1988) is also possible. Overall, the calculations are comparable.

6.5.2 Cumulative Permeation Solutions

Two checks were made with the CP code, "Crank424". The first was to compare the CP values from trapezoidal integration of the permeation rate data with the "Flux" code. This was comparable. The second was to compare graphed data with Figure 4.2 in Crank for a dimensionless plot of cumulative permeation (CP) against time. The plot appeared identical to the published plot.

By using the cumulative permeation curves rather than permeation rates to calculate permeation indices, noise in experimental data tends to cancel and a smoother curve results. This makes comparisons of experimental data with theoretical permeation curve shapes more precise.
SECTION 6.6 EFFECT OF DETECTION LIMIT ON BT AND LT

6.6.1 Introduction

Schwope et al. (1988) found that the LT derived from integrating an open loop permeation rate curve to give the equivalent closed loop permeation curve was not the same as a LT from a measured closed loop experiment. Schwope et al. (1988) stated that the "procedure is not appropriate". For their permeation curves, each measurement below the permeation rate analytic detection limit (DL), appeared to be have been recorded as zero, and thus the integral was underestimated and the LT estimates were in error. Their contention appeared to be confirmed by re-calculation of the CP in Figure 82, using the same data as Schwope et al. (1988).

![Figure 82](image.png)

**Figure 82** Effect of BT on measured CP in open loop systems

The CP curve for a BT at 480 minutes (8 hours) produced a LT of 480 minutes and was greatly affected by the DL. The CP curve "BT 7" with a DL of 1E-15 μg cm\(^{-2}\)min\(^{-1}\) was effectively the same as the "Fick's Law" curve in Schwope et al. (1988), with a DL very close to zero. The mathematical precision of the calculating engine in Excel prevented accurate calculations at a much smaller DL.

However, the contention that LT calculations from open loop permeation data are inappropriate is re-examined in the subsections below, as open loop permeation testing is common, and the LT permits estimation of the diffusion coefficient.
When the detection limit is low, such as for "BT 7" minutes in Figure 82, the BT value will be smaller than the LT value. As the DL increases, such as for "BT 480" minutes, the curved part of the curve has disappeared and the measured BT value is the same as the measured LT value. The measured BT value will asymptotically approach the measured LT value.

6.6.2 Detection Limit Modelling Experiment
Although BT is widely used and LT has some acceptance, there has been no direct comparison of the effect of detection limits on these indices. The following work was performed to determine this relationship.

Permeation Rates were calculated using Standard Conditions and the BT was calculated by iteration for a series of permeation rates. The CP was calculated by trapezoidal integration of the PR curves to derive LT values, just as if the data were from an open loop permeation experiment. Mathematically, this was performed using the Intercept function in Excel (which performs a least squares regression estimate of the intercept) to derive the LT.

To allow comparison of calculated BT and LT at various detection limits, values were normalised to the ASTM F739-1996 nBT permeation rate of 0.1 $\mu$g cm$^{-2}$min$^{-1}$. This approach is not quite rigorous, as a nBT for 0.1 $\mu$g cm$^{-2}$min$^{-1}$ requires that the analytic detection limit be below this figure, with allowance (2 or 3 $\sigma$, depending on the distribution of the background signal, for $p<0.05$) for scatter of the zero permeation rate measurement. If this scatter is zero, as is presumed here, then the detection limit and the minimum detectable permeation rate are the same.

For $D = 2.5E-6$ cm$^2$min$^{-1}$ and $L = 0.05$ cm, the calculated LT is 167 minutes, giving true SSPR conditions Crank (1975) at 3 x LT of 500 minutes.

6.6.3 Results of Detection Limit Modelling Experiment
In Figure 83, BT and LT values have been presented as a percentage of the values derived for a DL of 0.1 $\mu$g cm$^{-2}$min$^{-1}$ to give a common 0 to 100 scale and plotted against a range of detection limits (as a percentage of the steady state permeation rate). If the DL had no effect on BT and LT, then a horizontal, "no effect line" at 100% would result.
Figure 83 demonstrates that BT is very dependent on the analytic detection limit (DL in units of permeation rate, $\mu g \ cm^{-2} \ min^{-1}$), but the dependence of the LT on DL is weak. The choice of BT is very arbitrary, and is largely determined by the DL, so in itself, BT has very little direct toxicological meaning. As already noted, the LT is derived by extrapolating the steady state permeation portion of the integral of the open loop permeation curve back to the time axis, so it is largely independent of the DL. In fact, as stated before:

$$L T = \frac{l^2}{6D} \ 	ext{which implies}$$

$$P = \frac{lS}{6LT},$$

so LT is inversely proportional to P (or SSPR). However, what is recorded as LT is the first instance of permeation, once the true LT is exceeded.

The permeation rate rises quickly to a SSPR, so if the permeation rate DL is 50% of the SSPR, then most of the integral is determined by the permeation curve, not the DL. In this case (DL is 50% of the SSPR), the error in LT is 14%. Even a DL of 70% of the SSPR gives a LT error of only 33.6%, which is acceptable when compared with the scatter of published BT values in ASTM F739-1996 where the acceptance limit at 2.8 CV was 74% for nBT between laboratories for acetone – reference neoprene. (It could
be assumed that in selecting gloves, then gloves tested by different laboratories could be ranked, so inter-laboratory variations rather than intra-laboratory variations are used here.

### 6.6.4 Discussion of Detection Limit Modelling Experiment

Schwope *et al.* (1988) were correct in indicating that the analytic detection limit affects estimates on open loop derived LT's. However, in practice, the error is acceptable, even when the detection limit is half of the SSPR. Visually, if there is some curvature at the bottom of the CP curve, then the LT estimate will have acceptable error. Schwope *et al.* (1988) plotted a CP curve with a BT of 480 minutes (8 hours) with a DL of 2.4 μg cm\(^{-2}\) min\(^{-1}\), which is over 98% of the SSPR. Data with such a low level of analytic sensitivity would be suspect and difficult to replicate. The detection limits are shown in Figure 84.

![Figure 84 Detection limits used by Schwope *et al.* (1988)](image)

Contrary to the view of Schwope *et al.* (1988), adequate LT estimates may be made using open loop permeation testing, except when the DL is close to the SSPR. This limitation was not made clear by Schwope *et al.* (1988).
SECTION 6.7 FITTING ANALYTIC SOLUTIONS TO EXPERIMENTAL DATA

6.7.1 Introduction
Permeation indices such as LT have been derived from CPC permeation data with the assumption that the permeation curves may be represented by a model of Fickian diffusion with constant D, and that the LT can be used to derive fundamental parameters like D. As the product of D and S/l is the permeation rate, S may also be estimated. It is appropriate that an analytic solution be used to test this assumption.

The analytic solutions were fitted to two sets of experimental data. The first was for acetone vapour with reference neoprene. A good fit was not expected, as permeation models using a simple fixed diffusion coefficient are known to produce a poor fit with rubbery polymers (Crank, 1975; Neogi, 1996). Both linear and exponential dependence of D on the concentration of the solvent in the polymer have been used to fit Fickian models to experimental data. An exponential dependence of D on concentration gives the appearance of a time delay for the onset of the permeation process (Uchytil et al., 1996). However, other processes such as the filling of the volume between polymer chains can also produce similar curves and could explain the process, keeping D constant.

A second set of data was derived from trials with acetone through Tedlar from a disused sampling bag. These bags are used in occupational hygiene to collect air samples and to generate test atmospheres. Here, a relaxation process could be expected (Crank, 1975), as stresses caused by the solvent take time to dissipate. If the relaxation was completed after permeation was detected, then a change in the permeation rate, perhaps by an order of magnitude could be expected (Uchytil et al., 1996).

6.7.2 Experiments Fitting Analytic Solutions

Fit of analytic solution to acetone-vapour vs reference neoprene data
The permeation curve for liquid acetone vs reference neoprene has already been presented to calculate LT. An acetone vapour - reference neoprene permeation curve was produced using the Griffith Mk2 Intermittent exposure cell (Chapter 8), by leaving the wetting and purge mechanisms disconnected and exposing the test sample to acetone vapour from the cell reservoir. This arrangement could be expected to reduce the effect of swelling as the acetone concentration was reduced at the surface of the sample.
The acetone vapour permeation curves are shown in Figure 85, together with a calculated permeation curve based on estimates of D from the LT (see Equation 3 on page 1) and adjusting the SSPR in the solution to give similar SSPR. This was performed using the “Goal Seek” facility in Excel’97 to adjust the scaling factor. This adjustment permitted an estimate of $S/l$ as the permeation rate, $P = D \times S/l$.

Figure 85 Fit of solution to acetone vapour – reference neoprene permeation curve

Despite the lower concentration of acetone at the surface of the reference neoprene, the fit of the analytic solution to the curve was still poor.

**Fit of analytic solution to acetone vs Tedlar data**

Acetone permeation data from permeation trials with acetone and Tedlar® from an SKC sample bag used to generate test atmospheres are presented in Figure 86 on a linear scale as cumulative permeation. It is shown in Figure 87, but as a permeation rate on a logarithmic scale to highlight the early data.
The LT was calculated from the linear portion of the graph and used to estimate D for the steady state phase of the process. The low values for the calculated curve in Figure 86 are due to the low estimate of D. The permeation pattern before 40 minutes is not visible with a linear scale but detail is revealed by a plot on a logarithmic scale, and the disparity between calculated and measured nBT values becomes apparent in Figure 87. Here, permeation rate rather than cumulative permeation is plotted to highlight the changes in the experimental permeation curve.

When D was calculated from a LT (52.3 min) derived from the permeation rate, the predicted nBT (at 0.1 μg cm⁻²min⁻¹) was 10 minutes, but the experimental nBT was 40 minutes. The permeation curve is complex, but at least two stages are apparent in the permeation process. This might be due to a swelling of the polymer matrix by the...
solvent. Only once the entire polymer is swollen, does the permeation rate increase. This may be pictured like a huge number of doors along a corridor being opened. Only when all the doors are open does the traffic (permeation) flow at a higher rate. This could account for the inflection at 40 minutes. The curve is not explained by a simple constant value of D and Fickian Diffusion.

6.7.3 Discussion of Fit of Analytic Solutions to Model

The fitted D and S/l values for both acetone liquid and vapour challenging reference neoprene are given in Table 19. The D was calculated from the Lag Time and the S/l value from the SSPR and assumed D and S were constant during the permeation process.

Table 19 P, D and S/l for acetone vs reference neoprene

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Liquid</th>
<th>Vapour</th>
<th>Liquid to Vapour Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (μg cm⁻²min⁻¹)</td>
<td>200</td>
<td>1.7</td>
<td>118</td>
</tr>
<tr>
<td>D (cm²min⁻¹)</td>
<td>0.004384</td>
<td>0.007664</td>
<td>0.6</td>
</tr>
<tr>
<td>S/l (μg cm⁻²)</td>
<td>1617.934</td>
<td>8.817667</td>
<td>183.5</td>
</tr>
</tbody>
</table>

The solubility per unit thickness (S/l) of acetone in the neoprene is 60% of the value expected from a ratio of the molar volumes of acetone vapour and liquid (2.24E4 mL vapour: 74.05 mL liquid = 302. Any concentration dependence D is relatively small compared to the effect acetone concentration had on S.

For acetone permeating Tedlar, the pattern is more complex and the model predicts a much earlier breakthrough of acetone.

It was not possible to generalise the inability of LT estimates to produce accurate models of permeation with constant D and outside the scope of this work. However, some published data was available to compare with the neoprene data.

Published permeation model data

The only comparable published fit of permeation models to CPC data was for acetone with rubber (Goydan et al., 1988a). This is shown in Figure 88. The data were digitised from a figure presented by Goydan et al. (1988a) and the shape of the calculated curves will be considered. Goydan et al. (1988a) noted that the applicability of their solution depended on the accuracy of calculation of D and S, and the applicability of Fick's law, and an assumption of constant D.
In Goydan et al.'s (1988a) data, there are three sets of experimental permeation curves B1, B2 and B3 shown as symbols. The solid curve labelled "UNIFAP" used a generic structure for the polymer and permeant to calculate the curve. This approach took into account functional groups and adjusted for permeant and polymer chain length, to estimate S and D. The curve labelled "Kumar" used an Equation of State approach for calculating S and D. In both cases D, was corrected for the molecular weight of the permeant. The "Kumar" solution, scaled by 17.2 was re-drawn (with dots joined by a line) to make it comparable with the UNIFAP solution.

The shape of the calculated permeation curves for both the simple solution for acetone vapour (Figure 85) and Goydan et al.'s (1988a) solutions that used more complex derivations of D and S (Figure 88), were similar. Both predicted an increase in permeation sooner than was measured. The experimental data was delayed in both approaches, only to rise steeply to steady state values.

**SECTION 6.8 CONCLUSIONS**

- Breakthrough Times are extremely sensitive to analytic detection limits, whereas Lag Times are remarkably insensitive, even when the detection limit is 50% or more of the Steady State Permeation Rate. Thus, the integral of an open loop permeation curve to give Cumulative Permeation is appropriate for calculating Lag Time.
• Simple analytic solutions for permeation with a constant diffusion coefficient and constant solubility, fell short of completely describing the permeation of acetone through reference neoprene under conditions of continuous exposure. This limitation appeared even greater with acetone vs Tedlar and failed to predict a two-stage permeation process.

• Caution appears warranted in applying solutions based on estimates of the diffusion coefficient from Lag Times to estimate toxic exposures before steady state permeation occurs.

• It appears that the fit of permeation models to permeation data requires more attention to discern the nature of the permeation process. The precise measurement of LT does not infer confidence in estimating D.

• There is reason for caution in applying the findings from permeation models to predicting toxic exposures in the workplace, particularly in the transition phase before steady state conditions develop.
CHAPTER 7. A PERMEATION CELL FOR DIFFICULT-TO-TEST CHEMICALS

SECTION 7.1 AIM
This chapter describes the design, construction and testing of a novel cell using Attenuated Total Reflectance (ATR) to measure the permeation through CPC of difficult-to-test chemicals including those with low water solubility, low vapour pressures and solids, to circumvent the need for a collecting fluid.

SECTION 7.2 INTRODUCTION
The accepted approach codified in ASTM F739-1996 for the measurement of permeation of chemicals through chemical protective clothing (CPC) has been to use a cell with the challenge chemical on one side and a collection medium, either water or a gas like nitrogen, on the other side. The collecting medium is sampled to give an indication of BT and to measure the rate of permeation, usually given in $\mu$g cm$^{-2}$ min$^{-1}$. This approach has limitations when the chemical is poorly soluble in water or has a low vapour pressure.

The Griffith Mk2 cell was an evolutionary improvement on the Griffith cell, particularly with its superior collecting flow pattern. However, the approach to measuring permeation through CPC was much the same as most other two-chambered permeation cells. An alternative approach is to bring the chemical detector into contact with the test sample and measure the permeating chemical at or near the "inside" surface of the test sample. This eliminates the need for the permeant to evaporate into a gas stream or to dissolve in a collecting medium. In this state it is may be considered available for transfer to the skin of the user.

Effectively, the last 2 $\mu$m of the sample becomes the collecting volume, but with the disadvantage that it eventually saturates with permeant. This thickness is insignificant as most gloves are at least 50 $\mu$m thick and ASTM F739 (1996) only requires measurements to 20 $\mu$m.

The wide availability of Fourier Transform Infrared (FTIR) spectrophotometers, powerful personal computers and the development of FTIR software has made FTIR a practical method of measuring permeation of chemicals through CPC. Attenuated Total
Reflectance (ATR) is a standard FTIR method that has been applied to polymer analysis. It requires a test sample to be placed in intimate contact with a crystal. Light reflected inside the crystal penetrates the surface of the sample, giving a reflectance spectrum of a very thin layer of the otherwise opaque sample.

“Cumulative permeation” is determined at the crystal surface using the optical absorption spectra of the challenge chemical, as the concentration of the chemical is proportional to the optical absorbance at an appropriate infrared peak. While not all the chemical measured has “desorbed” from the CPC material, all the chemical measured is either on the “inside” surface of the CPC material, or within 2 microns of this inside surface. Direct transfer of (fat soluble) polychlorinated biphenols from the inside of PVC gloves to the skin was noted by Perkins and Knight (1989), so evaporation or dissolving in sweat is not a prerequisite for exposure.

As most workplace chemicals have an infrared "fingerprint", the ATR approach has the potential to be widely applicable. A novel permeation cell has been developed to permit a detection system based on FTIR-ATR to interface directly with a test sample with little or no sample preparation.

### 7.2.1 Depth of Penetration of Light into Test Sample

When light is reflected from the crystal surface, a necessary result of the boundary condition imposed by the surface is an exponentially decaying wave into the polymer.

![Figure 89 Evanescent wave in polymer (after Fieldson and Barbari, 1993)]

For total internal reflection, the refractive index of the "rarer" medium, in this case a polymer sample, must be less than that of the crystal. In general, the refractive index of polymers is about 1.5 and the refractive index of ATR crystals is greater than two.

This evanescent wave into the polymer may be expressed as the electric field $E$ at a distance $z$ into the inside surface of the test sample (Fieldson and Barbari, 1993)
\[ E = E_0 e^{-\gamma z} \]  

\text{Equation 21 Evanescent wave penetration}

Where

- \( E \) electric field at depth \( z \) in the sample
- \( E_0 \) electric field at surface of ATR crystal
- \( \gamma \) gamma, a constant (see below)
- \( z \) the distance into the sample

The constant \( \gamma \) is given by

\[ \gamma = \frac{2n_2 \pi \sin^2 \theta}{\lambda} \left( \sqrt{n_1^2 - \left( \frac{n_2^2}{n_1^2} \right)} \right) \]  

\text{Equation 22 ATR gamma}

Where

- \( n_1 \) the refractive index of the sample
- \( n_2 \) the refractive index of the ATR crystal
- \( \theta \) the angle of incidence of the reflected light
- \( \lambda \) the wavelength of the light

For \( n_1 = 1.5 \) (neoprene), \( n_2 = 2.4 \) (ZnSe), \( \theta = 45^\circ \) and \( \lambda = 1718 \text{ cm}^{-1} \) (C=O stretch in acetone), \( \gamma \) is 0.86. This value determines the depth profile of the evanescent wave as shown in Figure 90. A relative intensity of \( 1/e^2 \) or 13% determines the effective depth of penetration of the evanescent wave (Fieldson and Barbari, 1995) which in this case is just over 1 \( \mu \text{m} \).
Thus, only acetone in the last micron of the neoprene would be detected. This has a twofold significance. Only the acetone which has permeated through the entire thickness \((400 \, \mu\text{m})\) of the CPC sample is measured. Secondly, separation of the neoprene from the ATR crystal due to swelling, even a fraction of one micron, would reduce the light absorbed by the acetone in the neoprene and change the spectrum.

**SECTION 7.3 PROTOTYPE ATR PERMEATION CELLS**

To measure permeation of a chemical through a test sample, a cell is required to hold the challenge chemical on one side and keep the sample in contact with a horizontal ATR crystal. Any permeant would be detected at the crystal interface without the need for a collecting medium.

The concept was tested by building a prototype cell from a Griffith cell body clamped to a CPC sample on a flat horizontal ATR crystal plate (Perkin Elmer, zinc selenide crystal) as shown in Figure 91. The optics required to direct the infrared beam into the ATR crystal were below the crystal.
A pressurised version (Bromwich, 1997) using the Griffith Mk2 cell body allowed the cell to be gas pressurised to keep the sample in contact with the ATR crystal (Figure 92). The ports at the top would also permit a flow of a test gas through the cell with this gas pressurising the cell. In this case, a correction would need to be made for the increased concentration of the challenge gaseous chemical.

Only limited trials were performed with the unpressurised Griffith Mk1 ATR cell, as the aim was to investigate whether the approach would work. Scans were manually triggered at intervals on a Perkin Elmer 2000 FTIR set at 4 cm\(^{-1}\) and averaged over 4 scans. Care was taken during the assembly of the cell to ensure that the reference neoprene sample lay flat on the crystal. The background spectrum of the reference neoprene was taken before the addition of acetone. Thus, any the spectral peaks that evolved related to the acetone.

### 7.3.1 Results of Trials with Griffith Mk1 ATR Cell

The successive transmission spectra of the acetone are shown overlaid in Figure 93. The main absorption peak is due to the carbonyl (C=O) stretch at 1736 cm\(^{-1}\). The peak
values were extracted at this value and their inverse gave the absorbance values for calculating the cumulative permeation curve. The background spectrum for neoprene is also shown.

![FTIR ATR spectra](image)

**Figure 93 Sequential FTIR ATR spectra of acetone permeating reference neoprene**

This experiment demonstrates that the ATR approach had potential. There were concerns as to whether the sample remained in contact with the ATR crystal, as swelling of the neoprene would have occurred. This led to the development of design criteria for an improved ATR cell and construction of a cell to meet these design criteria. This cell was no longer used for permeation testing as it was too easy to damage the (expensive) ATR crystal. In this form, the permeation rate could not be directly calculated, but an estimate of the BT, but not nBT could be made.

**SECTION 7.4 DESIGN CRITERIA FOR PRESSURISED ATR PERMEATION CELLS**

The following set of design criteria was developed for a pressurised ATR permeation cell, based on the experience with the prototype ATR cells derived from the Griffith cell and the Griffith Mk2 cell bodies.

1. **The cell should be capable of being used with solids, liquids or gases.**
   
   This infers that the sample chamber must be readily accessible for loading and removing test chemicals, particularly solids. For solids, the sample chamber should be accessible after assembly of the cell with the test sample, so that the sample can be introduced at a precise moment at the start of the trial. Introduction of a test
sample during the assembly of the cell introduces uncertainties as to the start of the permeation process.

2. **The cell should be capable of being pressurised to keep the test sample against the ATR crystal.**
   
   This requirement comes from the need to analyse formed samples. Samples pressed into the crystal with heat or formed by evaporation of a solvent could have very different properties from samples taken from CPC. Laminated samples would have to be obtained from formed CPC material, such as 4H or North Silver Shield gloves.

3. **The cell must be quick to use and permit decontamination before disassembly.**
   
   The assembly has to be capable of being sealed and opened with the sample in place. This is a toxicological consideration, as toxic chemicals should be handled in fume cupboards, where toxic and corrosive chemicals circulate in the air before being extracted. This requirement precludes cells that include the ATR mirrors, as damage to the mirrors could result from liquids used to decontaminate the cell prior to disassembly, or from the test chemical itself.

4. **The cell must be capable of being kept at a set temperature to provide temperature gradients across the test sample.**
   
   Temperature regulation emulates the heating caused by a hand or the workplace. This requires separate heating modules on the two sides of the samples. If the temperature of the FTIR sample chamber is elevated, then cooling of the cell would be required to attain the required test temperature.

5. **The cell design should not damage the existing ATR assembly**
   
   As commercial ATR assemblies are expensive, modifications to the assembly are not desirable. Simple bolt-on adaptations were sought.

7.4.1 **The Griffith ATR Permeation Cell**

   A gas pressurised ATR permeation cell offers the advantage of allowing finished garments to be tested, including laminates. Conventional approaches to investigating polymers with FTIR-ATR have involved forming a sample on the crystal by polymer melts and evaporation of solvent from polymer solution (Balik and Simendinger, 1998). Such techniques would produce samples with different properties to those of the finished CPC garment.

   There were several constraints on the design of the Griffith ATR permeation cell. The Perkin Elmer ATR crystal reflects the light twelve times, and it is at these points that the evanescent wave occurs. In practice the sample has to cover the whole ATR crystal to
not only cover these active points but also to ensure that the edge of the test sample is sealed against the holder plate of the crystal rather than the crystal itself, to reduce the risk of mechanical damage to the crystal. This sealing is in addition to the close fit between the sample and the ATR crystal.

The construction of the Griffith ATR permeation cell is shown in Figure 94.

![Figure 94 Griffith ATR permeation cell (simplified)](image)

The heater wire (in a milled slot in the base), water channels (for heating or cooling water in the body) and bolts, are not shown in the figure to maintain simplicity. A number of materials were used and a numerically controlled milling machine used to precisely shape the components.

The cell base, with a built-in electrical heater, is made of aluminium for ease of machining and to ensure good heat transfer. It is easily unbolted from the ATR mirror assembly during decontamination. The channel construction aids heat transfer and simplifies alignment of the components. The ATR crystal, in its holder, sits in the channel and the infrared beam from the FTIR enters the ATR crystal though a slot in the cell base. The test sample is placed on the ATR crystal and the stainless steel cell body that holds the challenge chemical placed on the sample, sealing it with a ridge machined
in the bottom of the cell body. The cell body has internal channels for water to allow temperature control. However, in the trials, only the electrical heater in the cell base was used.

A 12-mm polycarbonate lid permits viewing of the sample and allows pressurisation (and the addition or flow through of liquid or gaseous chemicals) by the Festo pneumatic connectors screwed into the lid. This material has good chemical, temperature and impact resistance, but still has a limited life with strong solvents. The polycarbonate lid seals to the cell body with an O-ring held in a rounded rectangular groove in the top of the cell body. The design permits the cell to be assembled separately from the ATR mirrors, with the ATR crystal assembly sandwiched in the cell, but with the polycarbonate lid removable for the addition of chemicals. It also permits a primary decontamination of the cell at the end of a trial, after removal from the mirrors but prior to disassembly.

A critical element in the design was the 50 μm high, rounded rectangular ridge that sealed the cell body to the CPC test sample. This is not visible in Figure 94 but is shown in Figure 102. An O-ring seal was contemplated, but this may not have produced an optimum seal with compliant CPC samples.

SECTION 7.5 TRIALS WITH THE GRIFFITH ATR PERMEATION CELL

Trials were performed with acetone and naphthalene (a solid) using reference neoprene and a thin latex glove to determine the optimum pressure to apply to the cell and the effectiveness of the heating mechanism.

7.5.1 Effect of Gas Pressure

Varying the pressure gave changes to the baseline of the CPC spectra, and small changes in the intensity of individual CPC bands, which were consistent with an increased pressure causing better contact between the sample and the crystal. Gauge

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5 Much of Section 7.5 "Trials with the Griffith ATR Permeation Cell" is the work of Ms Kristina O'Callaghan, as part of her Honours program at the Queensland University of Technology's Centre for Developmental and Analytic Chemistry, under the joint supervision of Associate Professor Peter Fredericks and the author. These results have been published in two conference papers (O'Callaghan et al., 1998; O'Callaghan et al., 1998)
pressures of 0.6, 1 and 1.3 atmospheres were applied whilst observing the diffusion of acetone across 400 μm latex glove samples. Pressures over this range made no significant difference to the breakthrough time or rate of diffusion through the membrane.

### 7.5.2 Development of ATR Permeation Technique

In early trials, it was noted that, for some samples, there was a considerable increase in the background CPC absorbance for the time that pressure had been applied, indicating that contact between the CPC sample and the ATR crystal improved as the experiment progressed. It was concluded this was a result of air trapped between the ATR crystal and CPC sample, which slowly leaked out through imperfections in the crystal mounting under the influence of the applied pressure. The degree of increase in background CPC absorbance was not reproducible.

To solve this problem, the cell body was loosely fastened and the cell pressurised to remove the air between the sample and the crystal. The fastening of the cell was sufficient to permit a the seal between the Cell Body and the sample (better illustrated in Figure 102 on page 1), but loose enough for the air between the sample and the ATR crystal to escape. The pressure was then released, the bolts on the cell body tightened and full gas pressure applied. The background absorbance spectra then became reproducible.

### 7.5.3 Permeation Trials with a Solvent

The ability of the cell to measure the permeation of liquid permeants was tested by observing the permeation of latex, nitrile and reference neoprene by acetone and acetone in water mixtures. Figure 95 shows FTIR-ATR spectra collected as acetone was allowed to diffuse through reference neoprene sample at 20°C.
Figure 95 FTIR-ATR spectra of acetone diffusing through neoprene

Figure 96 shows the integrated carbonyl (C=O) stretching absorbance intensities for four replicates of this experiment. The optical absorbance is related linearly to the cumulative permeation in accordance with the Beer-Lambert Law (Urban, 1996). The curves in Figure 95 are, as expected, not straight as the accumulating permeant at the ATR crystal decreases the concentration gradient across the sample and decreases the permeation rate.

Figure 96 Carbonyl group absorbance, acetone and reference neoprene (1736 cm⁻¹)

7.5.4 Trials with a Solid

The FTIR-ATR approach to CPC permeation testing has the advantage that permeation by solids may be easily tested. Naphthalene (C₁₀H₈) was chosen as a convenient solid, as it is water insoluble and may be adsorbed through the skin and the reference
neoprene as the CPC material as it would make it easy for others to replicate this work. Table 20 was compiled from data given by Fricker (1992) in his PhD thesis, giving the permeation of nine solids “chosen to represent a range of vapour pressures and polarities” with 127 μm (5 mil) nitrile, natural rubber (latex), neoprene, PVC, polyurethane.

Table 20 Permeation of solids through neoprene, from Fricker (1992)

<table>
<thead>
<tr>
<th>Solid Compound</th>
<th>MW</th>
<th>Vapour Pressure (mm Hg @ 20°C)</th>
<th>Solubility (g/100mL in water)</th>
<th>BT (min)</th>
<th>SSPR (μg/cm²/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4-benzoquinone</td>
<td>108.1</td>
<td>0.1</td>
<td>1.5</td>
<td>45.0</td>
<td>3.21</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128.7</td>
<td>0.05</td>
<td>0.03</td>
<td>19.0</td>
<td>1.97</td>
</tr>
<tr>
<td>p-dichlorobenzene</td>
<td>147.3</td>
<td>0.4</td>
<td>0.008</td>
<td>6.4</td>
<td>3.16</td>
</tr>
<tr>
<td>p-nitrotoluene</td>
<td>137.1</td>
<td>0.12</td>
<td>0.005</td>
<td>14.2</td>
<td>5.03</td>
</tr>
<tr>
<td>Camphor</td>
<td>152.2</td>
<td>0.18</td>
<td>0.12</td>
<td>475.0</td>
<td>3.67</td>
</tr>
<tr>
<td>Phenol</td>
<td>94.12</td>
<td>0.36</td>
<td>8.4</td>
<td>21.0</td>
<td>2.01</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>110.1</td>
<td>0.001</td>
<td>7</td>
<td>31.5</td>
<td>9.05</td>
</tr>
<tr>
<td>4,6-dinitro-o-cresol</td>
<td>197.1</td>
<td>0.25</td>
<td>2.5</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2,4-dinitrotoluene</td>
<td>182.1</td>
<td>1</td>
<td>0.03</td>
<td>35.0</td>
<td>3.47</td>
</tr>
</tbody>
</table>

ND not detected

Naphthalene has a relatively high vapour pressure and its BT was one of the lowest. However, the SSPR for naphthalene through neoprene is the lowest of all the chemicals detected, making it a reasonable choice of test chemical. Naphthalene could be detected with the same HNU 101 PID used to detect acetone. However, as naphthalene is a solid at room temperature, contamination with a thin coating of naphthalene of all the plumbing downstream of a two chambered permeation cell, including the PID chambered permeation cell could be expected. Cells such as the ASTM F739 cell are unsuitable for solids as it would be difficult to hold the solid naphthalene in contact with the CPC sample.

A trial (Figure 97) was performed with the Griffith Mk2 ATR cell with naphthalene challenging a sample from a latex laboratory glove at room temperature (20°C). It shows the increasing absorbance at 780 cm⁻¹ due to the C-H bending vibrations of the naphthalene molecule. The naphthalene would have permeated as a vapour as the diffusion process is of individual molecules.
7.5.5 Trials of the Cell Heating Mechanism at Different Temperatures

The electrical temperature control facility was tested for the naphthalene-latex pair, using the same material (Figure 97). The integrated absorbance intensities for the C-H bending vibration as a function of time for duplicate trials at 20°C, 38°C and 45°C is shown in Figure 98.

![Figure 98 C-H bending vibrational absorbance for naphthalene permeation through latex at three temperatures](image)

The cumulative permeation (absorbance) increases with temperature and the BT decreases with temperature. The duplicate samples gave reasonable reproducibility. Unlike the acetone-neoprene curves (Figure 96), the naphthalene curves show no sign of
flattening. This may indicate that the build-up of naphthalene at the crystal was not significant and may be due to the low permeation rate of the naphthalene through the latex, due to the relatively large size of the naphthalene molecule.

Further work is planned by the author to determine the stability and uniformity of the temperature in the cell and on the surface of the sample.

SECTION 7.6 DISCUSSION

7.6.1 Scaling the Griffith Mk1 ATR Permeation Cell Data

There are practical difficulties in the direct method of scaling the sequential ATR spectra in Figure 93 to give cumulative permeation in the accepted permeation units. While it may have been possible to scale the cumulative permeation curve to \( \mu g \, cm^{-2} \) with serial dilutions of acetone in another solvent over the same area of the ATR crystal as the neoprene, this would have been difficult to achieve. Two methods of estimating the scaling factor for the cumulative permeation curve are based on the permeation rate curve from the Griffith cell validation experiments derived under identical conditions.

The first method, shown in Figure 99, gives a scaling factor of 16,600 to convert optical density to cumulative permeation of acetone (\( \mu g \, cm^{-2} \)). The rationale for this approach is that before significant build-up of acetone at the ATR crystal occurs, the transport processes inside the ATR permeation cell sample would be similar to those in the Griffith cell sample, so the slopes of the cumulative permeation curves should be the same. The slopes were matched in the time interval between 24 and 31 minutes. This approach ignores the delay between the curves and effectively matches the permeation rate over the period that both curves increase linearly. The reasons for this delay are discussed in subsection 7.6.2.
Figure 99 Scaling the ATR absorption curve by 16,600 to match Griffith cell CP curve

A second slightly different method (Figure 100) matches the maximum permeation rate of the derivative of the ATR permeation curve with the SSPR from the Griffith cell. A scaling factor of 17,500 was obtained by this approach, but fewer points were used for the match, making the match less certain. It assumes that steady state conditions occur before the permeation rate decreases.

Figure 100 Normalisation of ATR PR curve, scaling factor 16,600
It is evident that the ATR PR reached a maximum and then decreased. This may have been due to both the build-up of permeant decreasing the concentration gradient and to swelling of the polymer producing an air gap between the sample and the ATR crystal. BT times for the ATR and PID detectors are difficult to compare as the two detectors used would have different sensitivities. The detection limit for the Griffith Mk1 ATR cell may be greater than the nBT permeation rate of 0.1 $\mu\text{g cm}^{-2}\text{min}^{-1}$ as the ATR PR curve lagged the Griffith cell curve by about 6 minutes near the detection of breakthrough, indicating a delay in the detection of the solvent had occurred.

### 7.6.2 Comparison of Griffith Mk1 and Mk2 ATR Cells

By comparing the Griffith Mk1 and Mk2 ATR cells, the improvement in performance of the Griffith Mk2 ATR cell is highlighted. The data from the Griffith ATR permeation cell from Figure 96 has been scaled and overlaid on Figure 99 to give Figure 101. The four curves from the Griffith ATR permeation cell show a BT similar to that of the Griffith cell and have similar initial CP values. The Griffith Mk1 ATR cell has a BT 5 minutes later. The Griffith ATR permeation cell curves tended to flatten at similar CP values as the prototype ATR cell, but there were significant differences in the shape of the ATR curves between the two cells. All these factors are explicable if the lack of pressurisation of the prototype cell is considered.

With cell pressurisation (see 7.5.1), the sample is held in contact with the crystal, so an earlier breakthrough would be expected, as the better contact would allow the evanescent wave to penetrate slightly further into the sample. The difference in shape between the Griffith Mk1 ATR cell and Griffith Mk2 ATR cell curves may be due to a slight space between the sample and the crystal acting like a collecting volume. This collecting space for the Griffith ATR cell would have been minute, formed by small surface irregularities on the sample and crystal surfaces, as the sample was held by gas pressure to the ATR crystal. On removal of the gas pressure, the sample had to be peeled from the ATR crystal, indicating the absence of air between the sample and crystal and perhaps the formation of weak bonds. The bonding was greater with time. A greater concentration of chemical would build up on the "inside" surface of the sample, reducing the permeation rate earlier. However, the effective collecting volumes of both ATR cells was low, so similar equilibrium CP values would be expected.
The data does indicate that at least initial pressurisation was required to maintain contact between the test sample and the ATR crystal.

Figure 101 Prototype and Griffith ATR cell permeation data (acetone-neoprene)
7.6.3 Comparison of the Griffith ATR Cell with the Balik ATR Cell

The design of a remarkably similar cell for testing polymer films was published by Balik and Simendinger (1998) in the same month as the preliminary results of the Griffith ATR cell were obtained. These two gas pressurised ATR cells are compared in Figure 102. The detail of the metal seal in the Griffith ATR cell is shown in this view.

Very similar spectra could be expected with either. The Balik ATR permeation cell was designed for polymer scientists to test formed samples without melting or evaporating the polymer onto the ATR crystal, and thus preserves the polymer chain structure of the sample.

However, there are a number of features that are different:

- The Balik cell appears to require about twice the amount of chemical due to the greater width of the sample chamber and an O-ring seal. On the Griffith ATR cell, the corresponding chamber is a slot through the thickness of the stainless steel body that has almost the same area as the ATR crystal due to the metal sealing ridge.

- The Griffith ATR cell can be heated, with the aluminium base and stainless steel body being separately heated. This permits the simulation of temperature gradients created by the hand or workplace. The bulk of the aluminium base for good distribution of heat. In the permeation trials, only the electrical heater was
used. (Trials are planned by the author to determine the uniformity of the heating or and the actual sample temperature of the CPC sample.)

- The Griffith ATR cell was designed with predetermined design criteria that included the safety requirement to be able to load and clean the cell with the sample in place, but separate from the ATR assembly with mirrors. The cell body and ATR crystal holder can be removed from mirror assembly. This led to a separate cover for the pressurised slot in the body of the cell. (The construction of the Balik cell is such that the cell body clamps directly to the ATR assembly with mirror, so loosening the bolts that hold the cell together must be done with the mirrors in place.)

- The pressurised slot in the Griffith ATR cell permits the use of solids either in a preformed lump or as a powder. The Balik ATR cell has limited access to the sample due to the lack of a separate cover, though the Balik ATR cell is apparently capable of measurements on solids (Balik, 1998). The cover of the Griffith ATR cell bolts to the body and the body then bolts to the base. This permits the cover to be removed separately. The arrangement of the bolt holes and slots in the body and base is better shown in Figure 94.

### 7.6.4 Limitations of the Griffith ATR Permeation Cell

Though the cell fulfilled most of the design criteria, there were a number of limitations, which would affect its utility.

The cell would not be able to be used with chemicals that attack stainless steel, though other materials could be used for the cell body.

The technique is most applicable when the test chemical has absorbance bands that do not overlap with those of the CPC, however systems in which there is severe overlap may still be studied if multivariate calibration techniques are used.

During the trials, the polycarbonate cover became crazed and it was eventually replaced with a glass cover, with the inlet and outlet ports being moved to the cell body in a new version of the cell.

The trials on the prototype ATR cell demonstrated that the effective collecting volume was very small, limiting estimates of SSPR. More research is required with other
chemical – CPC combinations to determine how well permeation curves from two-chambered permeation cells compare with those using ATR cells. It may be possible to estimate the open loop SSPR from the ATR permeation curve by estimating the effect of build-up of permeant on the permeation rate. The concentration gradients inside the CPC sample would be expected to be similar to that through half the thickness of a sample exposed on both sides to challenge chemical. A solution to that problem is given by Crank (1975).

Though BT estimates may be made, nBT and SSPR estimates may be more difficult to obtain, as the absorbance units have to be expressed as $\mu$g cm$^{-2}$ and differentiated to derive both nBT and SSPR estimates. The trials with the prototype cell indicated that the PID measurements may be more sensitive than the FTIR-ATR measurements, as the ATR data lagged the Griffith cell data (Figure 101). Measuring a $0.1 \ \mu$g cm$^{-2} \text{min}^{-1}$ permeation rate to estimate the nBT may be require a more sensitive detector on the ATR spectrophotometer or further development of the technique.

Gas pressurisation of ATR cells may squash some polymers and reduce their thickness. This was seen as a limitation of the cell developed by Ehntholt et al. (1990) in attempting to keep contact between the test sample and the silicon rubber collection media with a plunger. Rubbers are almost incompressible with a Poisson ratio of almost 0.5 (see Glossary), so unless the CPC material was particularly spongy, uniform pressure should have little effect on the test sample. In practice, the pressure required to hold the sample against the ATR crystal was in the order of an atmosphere (see 7.5.1), so compression of the sample was not a great concern. Much greater compression would probably be applied to a sample in clamping the sample in a permeation cell, though the effects of this pressure would mainly be on the clamped area. Tightening the clamping bolt on the Griffith Mk2 cell did produce a minute transient spike in the background permeation rate (Figure 79, page 1) so the effects of pressure on a sample, though small, are measurable.

Modifications could be made to the Griffith ATR permeation cell design to permit permeation testing under conditions of cyclic intermittent exposure. This could be done by inverting the cell and utilising the mechanism in the intermittent exposure cell designs in Chapter 8. However, it may be necessary to continue the gas pressurisation
throughout the process to maintain the contact between the CPC sample and the ATR crystal.

As mentioned in the literature review, interactions between the permeating chemical and the CPC polymer would be expected to produce changes in the infrared spectrum of the polymer. This has the potential to characterise the permeant-polymer interaction, but this investigation was beyond the scope of this work.

SECTION 7.7 CONCLUSIONS

- The gas pressurised Griffith ATR permeation cell was demonstrated to produce permeation data with a liquid (acetone) and a solid (naphthalene), showing the potential of the approach to measuring the breakthrough of otherwise difficult-to-measure chemicals under conditions of continuous exposure. Measurements of gases and vapours are also possible. The method is simple and fast, and promises a reasonable level of reproducibility, but the Griffith ATR cell requires testing with a range of solids (including granules) with different vapour pressures, water insoluble chemicals, and mixtures of chemicals, particularly agricultural chemicals, to test its full potential.
- Pressurising the cell with a gas holds the test sample against the ATR crystal, however more trials would have to be performed to determine whether this ability extended to a wide range of chemicals and CPC polymers. The low gas pressure in the cell may still compress very compliant samples.
- The electrical heater mechanism reliably heated the cell to temperatures in the range 20°C to 45°C, but the temperature of the CPC sample itself and the uniformity of heating the cell was not measured.
- The technique of pressurising the cell whilst loosely assembled to drive out air between the sample and the ATR crystal kept the sample against the crystal, even in the absence of the clamping pressure. This advance in the method is attributable to Ms Kristina O'Callaghan.
- BT's may be estimated from the raw ATR data, but it is difficult to derive cumulative permeation units of $\mu g \text{ cm}^{-2}$ from absorbance data and thence permeation in units of $\mu g \text{ cm}^{-2}\text{min}^{-1}$, so nBT and SSPR rates are difficult to calculate. Further development of the ATR theory and techniques for CPC permeation may permit an acceptable estimate of permeation rates in acceptable units.
• ATR permeation cell data may be approximated to closed loop permeation with a near zero collecting volume. This limits simple derivation of an open loop SSPR value as build-up of permeant at the ATR crystal reduces the permeation rate before conditions similar to steady state permeation with an open loop cell are reached. This limitation may not be significant in practice with molecules of low volatility, as a significant factor in their low volatility can be their molecular size that limits their diffusivity.
CHAPTER 8. CYCLIC INTERMITTENT EXPOSURE

SECTION 8.1 AIM
The aims of this chapter are to:

- construct a prototype automatic intermittent exposure cell (the Griffith Intermittent exposure cell);
- develop design criteria from experience with this cell;
- develop an intermittent exposure cell to meet these criteria (Griffith Mk2 Intermittent exposure cell); and
- compare the performance of the new cell against the only known intermittent exposure cell permeation data published in ASTM F1383-1996 "Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Intermittent Contact".

SECTION 8.2 INTRODUCTION
Most workplace tasks do not involve continuous exposure to chemicals, such as a worker standing still with gloved hands in a bucket of solvent. Testing using ASTM F739-1996 gives permeation data that represents such an exposure regime.

The literature review (Chapter 2) outlined some of the factors, such as exposure pattern, temperature gradients and mechanical stresses that can affect permeation. It is difficult to replicate combinations of any of these parameters in the laboratory, so the trend is towards the replication of individual parameters. To evaluate exposure patterns a standard intermittent exposure cell (ASTM F1383, 1996) has been developed. However the ASTM F1383-1996 cell is manually operated and as such is not suitable for unattended operation, making testing more expensive and less precise in the hands of inexperienced operators.

8.2.1 Simulation of Workplace Exposures
An indication of the expected permeation curve under intermittent exposure was given by ASTM F1383-1996 for acetone against reference neoprene. As samples of the same material had been made available by ASTM Committee F23, replication of these curves and accounting for any differences, were of interest. The published curves were scanned, digitised at the same marked data points and replotted in Figure 103. The one minute wet time and 15 minute cycle time are shown by the dashed line, "Wet".
The permeation curves appeared to have a non-zero permeation rate at the beginning, with significant variation (about 400% at 13 minutes, 36% at 28 minutes) in permeation rates between trials in the first thirty minutes.

SECTION 8.3 PROTOTYPE AUTOMATED INTERMITTENT EXPOSURE CELL

A prototype automated intermittent exposure cell (Griffith Mk 1 intermittent exposure cell) with associated hardware and software was developed by the author (Bromwich et al., 1997) and preliminary trials demonstrated that the approach appeared to work. Designs that relied on a gravity feed of test chemical, pumped flow (with a car windscreen washer motor) and a medical syringe injector were considered, but rejected, as they were mechanically unsatisfactory. The prototype was based on the Griffith cell and capitalised on the existing pneumatic control system in the GloveTest rig to produce the sample exposure, and gravity to drain the test chemical to a reservoir between exposures.
This cell is believed to be the first intermittent exposure cell design to permit automated, repeat exposures of CPC material.

Compressed gas pressurised the lower section "B" via port "A", and closed the ball valve "C". This forced the liquid test chemical from "B" along Teflon tubes "D" pushed onto stainless steel tubes "E" (made from hypodermic needles). The spray from "E" was directed at the test sample "F". The base of a Griffith cell "G" shown inverted on top of the cell, held the sample in place and allowed the permeant to be collected. Between exposures, the pressure was removed from "A" and the ball valve "C" opened, allowing the test chemical to drain back to "B". A series of brief exposure and drain cycles became the "wet" time (WT). The sample was dried by airflow through "H" to "J" for the "dry" time (DT). The WT followed by the DT constitutes an exposure cycle characterised by a cycle time (CT).

A limited number of tests were performed on the cell, but it was realised that the design was very much a prototype (e.g. various changes had to be made to make it work effectively and the return valve from a junk box could not be sourced commercially). A year after it was constructed, the first Standard incorporating an intermittent exposure cell was published (ASTM F1383, 1996).
SECTION 8.4 DESIGN CRITERIA FOR INTERMITTENT EXPOSURE CELLS

Design criteria were developed in Chapter 4 for cells for continuous exposure resulting in an improved design. These were used as a basis for additional criteria for intermittent exposure cells.

8.4.1 Additional Design Criteria for Intermittent exposure cells

The ideal intermittent exposure cell design would emulate realistic workplace exposures in a replicable manner. To allow the testing to be performed in the laboratory a simplified approach uses samples of the CPC garment. Although the ASTM F1383-1996 approach suggested the use of a manually operated glass cell, a more rugged, automated cell was an obvious evolutionary improvement.

The following design criteria, in addition to those for permeation cells for continuous measurement (Chapter 4) are proposed.

1. **External control over filling of cell.**
   The cell should be capable of being filled and emptied under external control to facilitate automation and precise timing of wet times. In addition, the sample should not be exposed to solvent vapour before the start of the trial. The mechanical disturbance of the test sample has the potential to be reduced by the design of the system to expose the sample. It is not known whether this factor is significant.

2. **The entire test sample should be wetted.**
   The cell should wet the entire exposed surface of the test sample. Ideally, this would occur instantaneously, or within a fraction of a second, which is difficult to achieve with manual filling. Without complete and rapid wetting of the sample, there are uncertainties in the timing of the cycles and additional variability in permeation data could be expected.

3. **Wet periods should be precisely and accurately controlled**
   The cell should be capable of keeping the sample wet for a predefined period by rapidly wetting the test sample at a precise time and keeping it wet for a precise time. When coupled with the rapid removal of the bulk of the test chemical at the end of a wet time, the period of exposure is more accurately and precisely known. The viscosity of the challenge chemical and its ability to “wet” the
sample will affect the rate at which it drains and the residual amount of challenge chemical that needs to be removed by evaporation.

4. **The drying flow must evaporate test chemical efficiently.**

The drying flow to evaporate traces of test chemical should ensure rapid removal of the test chemical so that the end of the exposure period is better defined. The effectiveness of this process will depend in part on the vapour pressure of the challenge chemical. Whether deliberate drying of the CPC is desirable is another matter, as it does not really represent what is likely to occur in the workplace. However, a known effect of any gas flow designed to remove challenge chemical vapour after wet periods is essential to reproducible and replicable results.

**SECTION 8.5 GRIFFITH MK2 INTERMITTENT EXPOSURE CELL DESIGN**

8.5.1 **Development of the Griffith Mk2 Intermittent Exposure cell**

The Griffith Mk1 Intermittent exposure cell fulfilled most of the design criteria, but the drying pattern was not well defined and it was a relatively complex design. A new design based on the Griffith Small cell was considered, but the design required too much machining and would have been difficult to decontaminate (see Appendix B). The design was discarded.

Several other designs, based on the Griffith Mk2 cell, were considered, to capitalise on the superior collecting flow of this proven design (see Appendix B). Nozzle and valve manufacturers (including agricultural, pressure cleaning, refrigeration, diesel, carburettor, pneumatics and air conditioning companies) were approached locally and around the world via the Internet for a miniature low pressure "solid cone" nozzle and a miniature return valve, but none could be sourced. A miniature agricultural nozzle (Riga) was sourced and tested but it required the test chemical to be ejected at much a higher pressure and only produced a "hollow cone" spray pattern.

The fundamentals of nozzle design were then investigated to develop a low-pressure miniature nozzle that wet the surface of the test sample. The graphics in Figure 105 show the actions of a number of nozzles and come from the Internet pages of Spraying Systems Co ([http://www.spray.com/techindex.htm](http://www.spray.com/techindex.htm)).
The nozzle design concepts were used to design a miniature nozzle for an intermittent exposure cell. Several miniature solid cone test nozzles were developed and tested. These had inserts that swirled the flow inside the nozzle just before the fluid hit a 1-mm orifice to produce a remarkably uniform spray pattern at 100 kPa. However, further nozzle development demonstrated that this complexity was not required. It was found that a simple nozzle similar to the solid cone nozzle in Figure 105, but without the swirling insert, wet the entire surface of the test sample at low pressure.

A straight 2-mm ID tube dipping into a reservoir was used with a 1-mm orifice in the end. A 200 milliseconds pulse of air forced liquid up the tube and through the orifice. This produced a small glob of test chemical that wet the entire exposed surface of the test sample without visible distortion. This was observed with a test jig and a transparent cellophane membrane and using water as the "solvent". A short program was written in Visual Basic to assist the optimisation of pulse length and draining time between pulses.

The pulse pressure-time characteristics were modified by permitting the air pulse to dissipate to atmosphere along an open tube. This limited the peak pressure exerted on the test sample and prevented undue pressurising of the test cell.

The new nozzle was integrated into a mushroom-shaped return valve and machined from solid Teflon®.
Figure 106 Integrated Teflon spray nozzle and return valve

Figure 107 shows the Griffith Mk1 Intermittent exposure cell and the new Griffith Mk2 Intermittent exposure cell, using an inverted Griffith Mk2 cell base as the upper part of the cell. The new cell had fewer parts and was easier to machine and decontaminate.

Figure 107 Griffith Mk1 and Griffith Mk2 Intermittent exposure cells

The dimensions of the cell were such that the cell could be used with the same heavy clamping frame developed for the Griffith Mk2 cells.

8.5.2 Operation of Griffith Mk2 Intermittent exposure cell

Figure 108 shows the operation of the Griffith Mk2 Intermittent exposure cell during the filling and cyclic wet, draining and dry cycles. The inverted Griffith Mk2 cell base has been left off for simplicity.
Figure 108 Operation of Griffith Mk2 Intermittent exposure cell

Two ports for filling and flushing the exposed volume are at "A"; the port providing the pulsed flow of air is "B" and the combined nozzle and valve is "V".

The four stages of the operation are:

**Filling**  A small funnel is attached to the "L" shaped stainless steel breather tube attached to the exhaust port at "A". The solvent enters the exposed volume and drains to the reservoir. Displaced air can escape through the pulsing port "B".

**Pulsing** A pulse of air is applied to port "B", pressurising the reservoir and causing the valve to lift, sealing the draining path to the reservoir. The pressure in the reservoir pushes solvent up the middle of the valve and through the nozzle, splashing a glob of fluid onto the test sample.

**Draining** The pressure in the reservoir is removed and the valve drops down permitting the solvent in the collecting zone to drain back to the reservoir through the cutaway parts of the nozzle-return valve.

**Drying** Nitrogen enters the eccentric inlet port at "A", creating a swirling, drying flow at the test sample. The nitrogen leaves by the outlet port at "A". During the drying cycle, port "B" is closed to prevent nitrogen from escaping through the reservoir, minimising evaporation of solvent in the reservoir.

The hardware associated with the intermittent exposure cell was more complex than that for the Griffith Mk2 cell and is shown schematically in Figure 109.
Figure 109 Block diagram of Griffith Mk2 Intermittent exposure cell flow controls

Code was written to command the *GloveTest* rig to expose a reference neoprene sample in the Griffith Mk2 Intermittent exposure cell with a series of pulses of acetone, followed by a short draining period to refill the reservoir. This was then followed by the drying period to complete the cycle. Most trials were performed with a wet period of one minute and a total cycle time between two and fifteen minutes. The permeation trial was performed as for continuous exposure, except that two extra lines were connected to the Griffith Mk2 Intermittent exposure cell. One line provided a drying flow of nitrogen and the other line controlled the pulsing of the solvent onto the sample and bled to atmosphere to limit the pressure in the reservoir.

The flow controls for the pulse to wet the sample were complex but did ensure that the test sample was not unduly pressurised and that the solvent evaporation during the drying period was minimised. Not shown in Figure 109 is the supply solenoid for the collecting flow popette valve, and the exhaust from the drying flow port which is hidden by the drying flow inlet port. If more than one intermittent exposure cell is used, the hardware in Figure 109 is replicated for each additional cell. If the cycle timings for the intermittent exposure cells are identical, than the pulse hardware is designed to be able to service all the intermittent exposure cells simultaneously. Only one cell was used in these trials.
If volatile chemicals like acetone were used, the reservoir of 3 mL would evaporate after about 3 hours, when the sample was wetted with acetone for one minute every fifteen minutes.

### 8.5.3 Griffith Mk2A Intermittent exposure cell

A modified version of the Griffith Mk2 Intermittent exposure cell with a larger reservoir, the Griffith Mk2A Intermittent exposure cell, was made for unattended trials extending over several days.

The reservoir was greatly expanded and the return valve was extended with a piece of Teflon tubing to account for the increased depth of the larger reservoir. The design depth of the extended reservoir was determined by the height of the clamping frame, and use was made of a prototype Heavy Frame with the locating lugs removed from its base.

![Griffith Mk2A Intermittent exposure cell in prototype Heavy Frame](image)

**Figure 110 Griffith Mk2A Intermittent exposure cell in prototype Heavy Frame**

A four channel thermocouple amplifier (Tain Electronics, Melbourne) for measuring surface temperatures of the test samples is shown in the background of Figure 110. A filling port that could be plugged was also added to the large reservoir. It was found that the additional volume of the reservoir did not affect the wetting pattern when a pulse of air or nitrogen was applied to the port "B".

### SECTION 8.6 INTERMITTENT EXPOSURE CELL TRIALS

This section is in two parts. The first part discusses some of the preliminary trials leading to the refinement of the testing protocols. The second part compares the results of the main trials with the ASTM F1383-1996 permeation data from shown in Figure 103. The experiments were maintained at 21±1°C.
There are limitations on the applicability of the results of these trials as only acetone and reference neoprene was used. Further experiments with less volatile, less polar and more viscous solvents are warranted to more fully demonstrate the capabilities of the Griffith Mk2 Intermittent cell.

8.6.1 Preliminary Trials with Griffith Mk2 Intermittent exposure cell

Experimental conditions

Experimental conditions were similar to that for the trials with the Griffith Mk2 cell, except that some challenge solvent evaporated at each drying time.

Trials were performed with a cellophane sample and a clamping frame used to visualise the collecting flow to adjust sample-wetting action of the cell. A drain time of 5 seconds was adequate to permit acetone to drain back to the reservoir between wetting cycles. A more viscous solvent may require a longer drain time. The amount and force of the wetting action was adjusted with a metering valve controlling the flow from the pulse solenoid, the width of the pulse and the length of tubing attached to the pulse bleed poppet valve. The drying flow rate was set at a between 50 and 200 mL min$^{-1}$, the wet time at 1 minute and the cycle time 15 minutes.

The sample was loaded as for trials with the Griffith Mk2 cell and solvent added just before the start of the trial to minimise any inadvertent solvent vapour exposure to the sample. A number of trials were performed with the Griffith Mk2 and Mk2a Intermittent exposure cells to permit the software and test rig to be adjusted, and determine the interval for replenishing the solvent.

Results of preliminary Griffith Mk2 intermittent exposure cell trials

Figure 111 shows the results obtained from exposing a sample of reference neoprene (Trial i60) to acetone. In this particular trial, the pulsing system was inadvertently not connected until 90 minutes after the acetone was added to the intermittent exposure cell reservoir. This still exposed the sample to acetone vapour. However, the results are presented as they reveal much about the cell and the permeation process. As discussed later, in subsection 8.6.3, this pre-exposure of the sample to acetone vapour also permitted direct comparison with ASTM F1383-1996 data. The legend in Figure 111 includes the code CT15 for cycle time 15 minutes and WT1 for wet time 1 minute. In this trial the drying flow rate was 53 mL min$^{-1}$. 

Chapter 8. Cyclic Intermittent Exposure
There are a number of features of interest in Figure 111. These were not immediately explicable. The letters A-G below refer to the labels in Figure 111.

A: The background is stable at 0.035 \( \mu g \ cm^{-2} \min^{-1} \), before

B: The addition of acetone to the reservoir. The level climbs slightly, perhaps due to an incidental splash of acetone during filling causing the release of undetermined contaminant (see Chapter 5)

C: The curve and then falls a small amount (the scale is logarithmic), perhaps as the solvent splash evaporates quickly, cooling the sample, and producing a lower background permeation rate, as the diffusion coefficient and solubility of any chemical or contaminant are temperature dependent.

D: As the membrane warmed, the background level, returned to "normal".

E: As the flushing mechanisms had not been connected, acetone vapour from the reservoir was allowed to build up next to the sample, allowing the vapour to permeate at a much lower rate than would be expected (Stannett and Yasuda, 1963) from liquid acetone exposure.

F: At 90 minutes the pneumatic lines for pulsing the solvent and drying the membrane were connected, and

G: The oscillatory permeation pattern similar to that published in ASTM F1383-1996 developed.
H: Associated with the oscillatory cycle was a glitch associated with the wet time. This glitch is discussed briefly in subsection 8.7.5 and further investigated in Chapter 9 as it did not appear in the ASTM F1383-1996 data.

8.6.2 Reproducibility with Trial i62 and Trial i67 Data

Two\(^6\) trials with the same cycle time and using acetone and reference neoprene are compared in Figure 112.

The experiment temperatures were within 1°C of each other and the collecting flow rates were close to 500 mL min\(^{-1}\). At this stage, the drying flow rates were not known to be a critical factor, but were set at approximately 200 mL min\(^{-1}\), but not monitored during the trials. The reproducibility (using the ASTM F739-1996 definition of reproducibility) for Cumulative Permeation (CP) values at 165 minutes is 9.9% (n = 2), less than 7.7% (n = 3) for the ASTM F1383-1996 intermittent exposure cell data at 60

\(^{6}\) More than two trials would have been desirable for each cycle time chosen, but the data for many trials was not directly comparable, due to timing problems in the GloveTest software. There was a conflict between a rigid timing schedule and timing that varied for each measurement cycle due to the increasing time to display successive data points. This data set was chosen as it represented “Standard Conditions”.

Figure 112 Reproducibility of data
minutes. The number of data sets is too small to properly compare the Griffith Mk2 Intermittent exposure cell and ASTM F1383 cell.

8.6.3 Comparison with ASTM F1383-1996 Data

**Trial i60 (equilibrated with acetone vapour)**

Plotting the data from Trial i60 from 90 minutes onwards (pre-exposed to acetone vapour to steady state conditions, then normal intermittent exposure) and the ASTM F1383-1996 data gave an almost identical plot (Figure 113). The calculated cumulative permeation data were 33.7, 33.9 μg/cm² for the longer ASTM trails and 36.15 μg/cm² for the i60 trial, a difference of 5.4%. The drying flow rate for the Trial i60 data was 53 mL min⁻¹ but unknown for the ASTM F1383-1996 data.

The initial permeation rate for the Trial i60 and ASTM F1383-1996 data were the same, suggesting the ASTM F1383-1996 data were also collected with the neoprene equilibrated against acetone vapour. The maximum permeation rates are similar, though the Trial i60 data shows a downward trend, whilst the ASTM F1383 data shows a slight upward trend.

**Trial i62**

A permeation trial was recorded with the same parameters as the ASTM data, a CT of 15 minutes and WT of 1 minute. The experiment temperature was a constant 21.8 °C, measured in the exhaust of the cell at the detector and the collecting flow rate was
550±4 mL min\(^{-1}\). The permeation curve, scaled down by a factor of 2.69, is shown with one of the ASTM F1383-1996 curves in Figure 114.

There were a number of differences between the data.

- The permeation rates from Trial i62 were about 2.7 times greater than that published in ASTM F1383-1996 and that found in Trial i60 (see Figure 113),
despite using neoprene from the same batch and using the same solvent. The reason for this difference remains unknown.

- The initial Trial i62 permeation rate was near zero but the ASTM F1383-1996 data were initially non-zero.
- Trial i62 data again contained a glitch, following the start of each wet time.

8.6.4 Trial with Griffith Mk2A Intermittent exposure cell

The extended run-time capabilities are shown in Figure 115 for the Griffith Mk2A Intermittent exposure cell, with a trial of 6 hours without refilling. The cycle time was 60 minutes with a one minute wet time.

Figure 115 Trial i69, cycle time 60 minutes

The circled region in Figure 115 shows a "glitch" from A to C, starting at the beginning of the wet cycle A. The glitch was repeatable but less pronounced than in the 15 minute cycles, but the decrease to a minimum permeation rate at B is more apparent. A new feature not apparent in the 15 minute cycle, was a rapid rise of the permeation from B to C. This may correspond to the evaporation of surface solvent and subsequent warming of the sample. Of significance is the position of the glitch relative to the timing of the wet cycle and beginning of the dry cycle, rather than at the peak of the permeation curve, as seen for the 15 minute cycle trials.

The peaks in the permeation curves were decidedly asymmetric as the increase in permeation following wetting of the sample occurred more rapidly than the decrease in
permeation as the test sample dried out. After two cycles or two hours, the cyclic pattern became repeatable.

Noise spikes, possibly from a poor electrical connection to the PID, occurred between 78 and 95 minutes. These have been numerically filtered by a median spike filter, five datum points wide (see Appendix D for details of the development and testing of the median spike filter).

SECTION 8.7 DISCUSSION

8.7.1 Design Criteria and Design of Griffith Mk2 Intermittent exposure cell
Design criteria for an automated intermittent exposure cell were developed and a cell that satisfied most of these criteria (at least for acetone with reference neoprene), was designed and constructed, based on the Griffith Mk2 cell with its superior collection flow characteristics. The design of the cell nozzle-return valve ensures the sample is instantaneously wet over its entire surface and the solvent is reused for subsequent cycles. The sample is not visibly stressed during the wetting or drying actions. Software and external hardware ensure that the wet periods are very precisely controlled and that the sample is dried between cycles.

It is not known whether the design criteria would be satisfied with less volatile solvents, or with more viscous solvents that may affect the wetting of the sample, solvent drainage and the operation of the return valve.

The additional design details from the continuous exposure cell that were not incorporated were optical transparency and high chemical resistance, both of which could have been incorporated with a greater cost of materials and machining. The cell is simple, has only one moving part and is easy to decontaminate.

The capacity of the solvent reservoir in the Griffith Mk2 Intermittent exposure cell is about 3 mL, sufficient for a three-hour trial with a volatile solvent like acetone. If the cell is filled with solvent some time before the trial, solvent vapour will evaporate and expose the sample to solvent vapour. Modifications to the support hardware ensure a flushing flow of gas through the wet side of the cell (the drying flow) to minimise this exposure.
8.7.2 Preliminary Griffith Mk2 Intermittent exposure cell trials

The Trial i60 data from the Griffith Mk2 Intermittent exposure cell showed a pattern nearly identical to that published for the ASTM F1383-1996 cell. As the Trial i60 data were for a sample equilibrated with acetone, the data strongly suggests that the ASTM F1383-1996 samples were also equilibrated with acetone vapour before the start of the trial. In the absence of this equilibration with acetone vapour, the shape of the permeation curve given by Trial i62 was very different, starting at zero and the oscillatory peaks developing more slowly.

No validation figures were available for the ASTM F1383-1996 intermittent exposure cell similar to those provided for the ASTM F739-1996 continuous cell.

8.7.3 Repeatability

When cumulative permeation was used to compare repeatability for the Griffith Mk2 Intermittent exposure cells, a standard error of 9.9% (n = 2) for two trials was calculated. Comparison of time-varying permeation rates with the ASTM data was difficult as the trials lasted for different times. When cumulative permeation for the time of the shortest ASTM F1383-1996 trial was compared, a standard error of 10.2% (n = 3) was calculated, but when the two longer trial were compared this improved to 1.7% (n = 2). The data for continuous exposure resulted in good repeatability with the Griffith Mk2 cell (se = 2.1%, n = 8, see Chapter 4). It could be expected that with refinement of the experimental technique, more repeatable data with the Griffith Mk2 Intermittent exposure cell could be obtained.

8.7.4 Effective Wet Time

If intermittent exposure is considered in terms of contact time, and the diffusion process is slow compared to the cycle time, then a simple scaling of the permeation curves would be expected. Thus the combination of a relatively slow diffusion rate and a short cycle of two minutes, with one minute wet would produce a relatively smooth permeation with little evidence of cyclic oscillation in a permeation curve scaled down by a factor of two. For a cycle time of 15 minutes and one minute of exposure, the permeation curve could be expected to scale down by a factor of approximately 15. The theoretical rationale for this is investigated in Chapter 10.

A better method of comparing the oscillatory patterns is to compare cumulative exposures, though care must be taken as just including or just missing a peak could
make a considerable difference if short trials are compared. The cumulative permeation for the Griffith cell validation data for continuous exposure is calculated to be 8.5 times that for the ASTM F1383-1996 intermittent data, though a figure closer to 15 would have been expected since the ratio of cycle time to wet time was 15 for the ASTM trials. If this difference is entirely attributed to the sample remaining wet with acetone more than the desired one minute, an effective wet time of 1.78 minutes results (1.78 = 15/8.5).

The formula used was

\[
\text{Effective wet time} = \text{wet time} \times \frac{\text{Fraction of cycle sample is wet} \times \text{CP continuous}}{\text{CP Intermittent}}
\]

............................. Equation 23 Effective wet time

Further work is required to determine whether this approach is valid. This could be determined in part by monitoring the drying flow for solvent. This would give a good indication of the presence of residual surface solvent, perhaps in the surface microstructure, either in microcracks and voids, or absorbed on the surface.

The Griffith Mk2 Intermittent exposure cell was designed to rapidly dry the test sample following a precisely timed exposure and the combination of automatic operation and good sample drying flow patterns should have given faster drying than for the ASTM F1383-1996 cell. This longer effective wet time may be due to the cooling of the sample at the beginning of the dry time thus reducing diffusion of the solvent to the surface of the sample. This factor was not further investigated.

8.7.5 Cyclic Glitch in Permeation Curves

The glitch that was apparent with the Griffith Mk2 Intermittent exposure cell data was not evident in the ASTM F1383-1996 cell data. The glitch occurred at the beginning of the wet time, followed by a rapid decrease in the permeation rate at the beginning of the dry time. It was initially thought that it was unrelated to the evaporative cooling of the sample as the temperature of the effluent gas appeared not to change. However, despite the lack of change in effluent gas temperature, measurements of the actual temperatures of the sample appeared warranted, as temperature changes from a warming effect of the solvent and evaporative cooling could explain the glitch and rapid decease in permeation rate. This is investigated in Chapter 10.
With respect to the ASTM F1383-1996 cell, a number of possible explanations for the absence of the glitch are suggested. The handling of the ASTM cell during emptying and filling of the cell may have made permeation measurement during this period inconvenient. The drying flow in the ASTM cell was less directed at the sample than in the Griffith Mk2 Intermittent exposure cell, so less efficient evaporation of the solvent would be expected. The drying flow rate was not given in ASTM F1383-1996, making further comparisons difficult. The choice of a 15-minute cycle may have also obscured the glitch, as the permeation rate was also falling at this time.

An additional explanation is that the glitch was simply missed due to the longer measurement interval between the ASTM data. There were 580 points plotted for Trial i60 in Figure 113, but a maximum of 82 points with the ASTM F1383-1996 data.

8.7.6 Griffith Mk2A Intermittent exposure cell
Modifications to the Griffith Mk2 Intermittent exposure cell to enlarge the reservoir permitted longer operation of the cell without refilling. No change to the performance of the cell was evident. However, the size of the reservoir made the simultaneous use of several of these cells difficult as only one could fit in a clamping frame at a time.

8.7.7 Simultaneous Testing of Multiple Intermittent exposure cells
Though a set of eight Griffith Mk2 Intermittent exposure cells was made, these were not used simultaneously in this work. A single poppet valve could produce the pulses to simultaneously wet each sample, but identical permeation data would not be obtained from each cell, as the measurements were sequential. To produce sequential pulses to each cell would have required two poppet valves per cell to provide the pulse and seal the reservoir during the drying time. In addition, additional channels on the programmable logic controller would have been required. Resources to permit this for eight cells were not available.

8.7.8 Suggestions for additional experiments
As noted in section 8.7.1, the use of only acetone with reference neoprene limits the degree to which it can be said that the design criteria have been met.

The following experiments are suggested to determine whether the design criteria can be met with a range of solvents and CPC materials.
Trials with less volatile solvents
Trials with a range of solvents with different volatilities would indicate whether the cell could produce well defined wet and dry times. Also, trials with other solvents with a similar evaporation rate but different polarity may show the influence if adsorption onto the surface of the CPC test sample in determining the wet and dry times.

Trials monitoring the solvent concentration in the effluent drying gas could be used to determine the "effective wet time" (see Chapter 9 for development of this concept).

Trials with more viscous solvents
The wetting of the solvent, drainage back to the reservoir and action of the return valve could be affected by the viscosity of the solvent. Trials with solvents of different viscosities would determine whether the mechanical clearances and nozzle design are adequate for general use.

SECTION 8.8 CONCLUSION

8.8.1 Meeting of the design criteria
An automated intermittent exposure cell, the Griffith Mk2 Intermittent cell was constructed to predetermined design criteria. The cell would have met the design criteria of the continuous cell (Chapter 4) and has met the additional design criteria for automated intermittent cells as discussed below.

Design Criterion 1. External control over filling of cell.
The sample could be wet under external control for predetermined lengths of time with acetone and water. Other solvents were not tested, but most solvents could be expected to have a low enough viscosity to drain to the reservoir and not affect the action of the valve. Solvents with the viscosity of honey would require very long drainage times.

Design Criterion 2. The entire test sample should be wetted.
This design parameter was tested with water and acetone. A very different nozzle design may be required with solvents that are more viscous. With greater viscosity and low wettability of a CPC sample, the wetting could be reduced. A different nozzle design would have to be contemplated if increased nozzle pressure did not increase wetting.

Design Criterion 3. Wet periods should be precisely and accurately controlled
The computer control of the valves controlling the values ensured the period during which the solvent was applied to the CPC sample and the period the drying flow operated were precise and accurate to within a fraction of a second. Care was needed in adjusting the pressure and duration of the pulse of air that pushed the solvent onto the CPC sample, to ensure complete wetting.

However, the time the sample remained wet, would depend on factors such as the volatility of the solvent and the drying flow pattern. This is further investigated in Chapter 9.

**Design Criterion 4. The drying flow must evaporate test chemical efficiently.**

The drying flow appeared to evaporate the solvent efficiently. However, less volatile solvents may not evaporate as quickly.

A further experiment monitoring the solvent concentration in the effluent drying flow would indicated the efficiency of the drying flow more directly.

**8.8.2 Other conclusions**

- The cell was tested against the permeation data from the ASTM F1383-1996 cell and gave near identical permeation curves with reference neoprene that had been pre-exposed to acetone vapour.

- Repeatability for the Griffith Mk2 Intermittent exposure cell appears to be less than for Griffith Mk2 cell as reflected by the greater spread of the permeation data. The published reference data were very limited and the intermittent exposure cell more complex than its continuous exposure counterpart. There is a need to investigate and standardise the factors causing the poor repeatability.

- The wet time for the ASTM F1383-1996 cell was 1 minute in a 15-minute cycle. However, the effective wet time, based on comparing contact time and resultant cumulative permeation rates for continuous and intermittent exposures, suggests a 1.8 minute wet time. Longer wet times were also calculated for the Griffith Mk2 Intermittent exposure cell, but the reason for this is unknown, as a better and faster drying of the sample was expected. It may be that the microscopic surface topography of the sample permits sheltering of trapped and adsorbed solvent in microcracks and voids.
• A significant glitch occurred in the data from the Griffith Mk2 Intermittent exposure cell data. This was thought to relate to warming of the sample from the solvent in the wet time and evaporative cooling at the start of the dry time.

• The lack of the glitch in the ASTM F1383-1996 data may be related to the different drying flow rate and flow pattern in the ASTM F1383-1996 cell, the manual operation of the cell and frequency of measurements. The choice of a 15-minute cycle may have also obscured the glitch in the ASTM F1383-1996 data, as it would have occurred at a time that the permeation rate was already falling.

• The Griffith Mk2A Intermittent exposure cell performed like the standard version, but greatly extended the time between refilling of the reservoir, permitting extended trials. It was not compatible with tests using multiple cells due to its size.

• The possibility of simultaneously measuring eight samples under conditions of intermittent exposure was not explored due to the need for additional hardware, but eight Griffith Mk2 cells were constructed to permit this experiment.

• There is scope for refinement of the test method and further direct comparisons with the ASTM F1383-1996 intermittent exposure cell.
CHAPTER 9. EFFECTS OF OPERATIONAL PARAMETERS ON CYCLIC INTERMITTENT EXPOSURE

SECTION 9.1  AIM

The aims of this chapter are to investigate new factors introduced by the use of this cell to test CPC and how these factors affect the permeation rate. This was achieved by investigations of

- the drying flow pattern, by comparing two variants of the intermittent exposure cell and modifying the drying flow pattern with a nozzle to direct the drying flow within the wet side of the cell and visualising the flow with dye;
- the drying flow rates in the absence of surface solvent, so that convective effects could be discounted;
- the drying flow rates in the presence of surface solvent, so that the effects of evaporative cooling could be studied; and
- the cycle time between exposures, as the only published permeation data, in ASTM F1383-1996 were for a fifteen minute cycle.

SECTION 9.2  INTRODUCTION

Permeation testing under conditions of continuous exposure used a constant concentration of solvent with time, essentially isothermal conditions and no drying flow. Because the existing temperature transducer on the collecting flow did not show a temperature drop in the drying time, a more sensitive temperature measuring system was needed to investigate evaporative cooling, with measurements of the temperature of the test sample itself. This issue was not addressed in ASTM F1383-1996, as it only required the temperature of the test cell to be measured. The drying flow rate was not specified.

9.2.1 Limitations of findings in this chapter

The experiments in this chapter were performed using acetone and reference neoprene so that the data could be replicated by others. However, there are limitations on the applicability of the data, and further experiments with less volatile and more viscous solvents are warranted.
SECTION 9.3 DRYING FLOW PATTERNS IN INTERMITTENT EXPOSURE CELL

9.3.1 Effect of Port Angle on Drying Flow Pattern
Two Griffith Mk2 Intermittent exposure cell bodies were constructed. One had drying inlet and outlet ports at 60° to each other (Figure 116). The drying gas from the inlet port was designed to flow across the middle of the cell and divide into two symmetric flows on the far wall of the cell. The other had the drying ports at 45° to each other, but the inlet port was offset by 10° from the centre of the cell. This offset was designed to direct the drying gas at an angle to the cell and produce a swirling flow, to maximise the mixing of the drying gas and scour the surface of the test sample.

The flows were visualised by filling the cells with water and injecting a red dye into the flow in the manner described in Chapter 5 for the collecting flow continuous cells. The water flow rate of 22 mL min⁻¹ was equivalent to 200 mL min⁻¹ nitrogen. The drying flow was made visible by replacing the sample with a thick clear plastic disk and clamping the intermittent exposure cell body in a frame such that the disk was visible. Figure 116 shows schematically the effect of drying port angle on the flow pattern from above. Only the wet side of the Griffith Mk2 Intermittent exposure cell is shown.

![Figure 116 Effect of drying port angle on flow pattern](image)

When the drying flow was straight across the cell without an offset of the inlet port, the flow divided into two nearly symmetrical patterns with little swirling. The dye cleared in about 8 seconds. With the drying flow was offset by 10°, a swirling flow resulted,
and the dye clearing in about 4 seconds. In both cases there was good mixing of the dye throughout the wet side of the cell, but the more rapid clearance was achieved with the eccentric drying inlet port.

### 9.3.2 Effect of Directing Drying Flow on Flow Pattern
To give more control over the flow pattern, a nozzle was machined from 5 mm diameter aluminium stock to enable the incoming flow to become more directional. The nozzle was screwed into the eccentric drying flow inlet port of the Griffith Mk2 Intermittent exposure cell.

![Drying nozzle](image)

**Figure 117 Drying nozzle**

Four directions of drying flow were investigated, clockwise, counter-clockwise, upwards towards the sample, and downwards away from the sample. Figure 118 shows these flows from above and side-on.

![Flow patterns](image)

**Figure 118 Effect of modifying drying flow pattern with a nozzle**

For the clockwise flow, the swirling pattern of the offset port was accentuated, but a similar flow pattern to that without the nozzle resulted. The major difference was that the flow swirled more. The counter-clockwise flow produced a pattern that was
surprisingly similar to the clockwise flow pattern, although it cleared the dye less rapidly. When the drying flow was directed upward towards the sample, a circular flow along the sample and then towards the valve predominated. There was good mixing. However, when the flow was directed away from the sample, there was a dead zone near the sample. Under these conditions, forced evaporative cooling could be expected to be least.

The eccentric drying flow in the Griffith Mk2 Intermittent exposure cell without a nozzle was close to optimal, and produced a good flow across the sample and adequate mixing in the rest of the cell. There appeared no need for additional direction of the drying flow.

SECTION 9.4 DEVELOPMENT OF A SAMPLE TEMPERATURE MEASUREMENT SYSTEM

Simple measurements of the temperature of the permeant from the cell were inadequate to reveal small temperature changes in the test sample due to the various forms of heat exchange between the test sample, the cell and the environment. These heat exchanges are detailed in Table 21, with redundant information being omitted. (e.g. radiative transfer between the collecting side and the test sample must be the same as the test sample and the collecting side.)
### Table 21 Heat transfer in a two-chambered intermittent exposure cell

<table>
<thead>
<tr>
<th>Transfer</th>
<th>Collecting side</th>
<th>Test Sample</th>
<th>Drying/Wet side</th>
<th>Cell Exterior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiative</td>
<td>Between sample and walls of cell</td>
<td>Between drying gas and walls of cell</td>
<td>Between cell and environment. Expect drying side to have greater heat transfer as it would cool more</td>
<td></td>
</tr>
<tr>
<td>Convective</td>
<td>Between drying gas and walls of cell</td>
<td>Between drying gas and sample</td>
<td>Between drying gas and walls of cell</td>
<td>Between cell and environment (air or water movement if in water bath)</td>
</tr>
<tr>
<td>Conductive</td>
<td>Between cell and clamping bolt and thence the environment</td>
<td>Between edges of sample and cell</td>
<td>Between cell and clamping frame base and thence the environment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Between sample and solvent during wet phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Between wetting and reservoir solvent during mixing in drain phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaporative</td>
<td>From permeant evaporating (relatively small)</td>
<td>From sample. Expect different rates between visible surface liquid, solvent in surface texture and solvent near surface (diffusion)</td>
<td>From wet walls of cell and leakage from reservoir</td>
<td></td>
</tr>
</tbody>
</table>

To model or measure all these heat transfers would be difficult, but it could be expected that the major routes of exchange that affect permeation would be evaporative cooling from the wet side of the sample, conductive exchange through the sample and evaporation of permeant from the dry side of the sample.

A contact sensor for measuring the temperature of the test sample needed to be small, to have a low thermal inertia and be located directly on the sample. The most economical approach was to use a thermocouple, but there were resource restraints in obtaining commercial multi-channel logging units. A non-contact infrared sensor used to measure body temperature by measuring the infrared emissions in the ear canal was considered, but not tried, as there were doubts about what would actually be measured.
9.4.1 Development of the Thermocouple System

Initially a laboratory thermometer with a thermistor was used to determine the temperature of the surface of the samples. The thermistor bead was positioned to sit against the test sample with a very slight pressure to ensure good contact, with some of the thermocouple wire also lying against the sample to minimise the effects of conductive heating or cooling along the thermocouple wire.

The laboratory thermometer had the disadvantage that each temperature reading had to be transcribed to make the temperatures match the permeation data. This was partially resolved by creating a software interface that permitted large temperature changes to be logged with a slider and changes of a fraction of a degree to be logged with a mouse click.

While these trials did show that the temperature changes on the surface of the sample during the wet and drying cycles were significant, the approach was quite unsuitable for extended trials as it was difficult to concentrate on manually logging the temperature changes for more than a few minutes. Too many measurement artefacts occurred.

Trials with a DVM and thermistor

A digital voltmeter (DVM, Protek 506) with temperature measuring and data logging capabilities had provision for a "K" type thermocouple. It had an RS232 serial port that could be interrogated with a PC. Visual Basic code was written to interrogate the DVM, extract the temperature information and time stamp it. This enabled temperature to be logged every two seconds without error, but only with 1 °C resolution.
Trials with this system gave repeatable changes of about 12°C on the wet side of the sample in the Griffith Mk2 Intermittent cell as the solvent evaporated. However, to properly measure temperature, the temperature of the collecting gas in and out of the cell, and temperature on both sides of the test sample needed to be measured simultaneously. An economical method of creating a multi-channel thermocouple amplifier was sought, utilising the spare channels on the A-D converter card. An additional card in the PC for a standard thermocouple interface would have produced software-addressing problems due to the number of other cards populating the PC.

**Trials with four channel thermocouple amplifier**

A number of suppliers were approached for a fast (better than 1 second) multi-channel temperature logging interface for the experiment. A four-channel thermocouple interface was developed by Tain Electronics, Melbourne (http://netstra.com.au/tain/). This was based on an LT1001 Precision Operational Amplifiers and a LT1025 Micropower Thermocouple Cold Junction Compensator (Linear Technologies http://www.linear.com), and using "T" type thermocouples. With practice, satisfactory thermocouples were made from "T" type thermocouple wire using an oxy-acetylene torch to melt the wires to a neat junction.

The four channel thermocouple amplifier interface gave better than 0.08°C resolution and the desired speed (many times per second, but limited by the software rather than an instrument) required for measurement of temperature changes in the Griffith Mk2 Intermittent exposure cell. Figure 120 shows the arrangement of the four thermocouples in the cell.
Figure 120 Thermocouples in Griffith Mk2 Intermittent exposure cell

Thermocouple "A" enters the cell via the stainless steel filling tube and is held against the wet side of the sample. Thermocouple "B" passes through the wall of the tubing for the collecting flow into the cell. Thermocouples "C" and "D" enter via the cell exhaust line to measure the temperature of the dry side of the sample and effluent gas temperatures respectively. This arrangement permits the simultaneous measurement of temperature changes in the collecting gas and across the sample.

**Calibration of thermocouples**

Four "T" type thermocouples and a "K" type thermocouple attached to the Protek 506 DVM were secured to the stem of a certified thermometer (Dobbie Instruments thermometer NATA Certificate 9606300, -10°C to 110 °C, 0.5 °C ± 0.15 °C, full immersion) in a 500 mL beaker with ice and distilled water. The temperature was ramped up at 1°C per minute from 0 to 40°C with a laboratory heater plate with a magnetic stirrer, and the temperatures of the thermocouples recorded. The standard thermometer temperature was manually logged with software controls similar to that used with the thermocouple instrument. This permitted a polynomial calibration curve to be calculated for each thermocouple and coded in the GloveTest software.

**SECTION 9.5 EFFECT OF DRYING FLOW RATE ON PERMEATION RATE**

Increased drying flow rate could be expected to enhance evaporation and decrease the temperature of the sample through evaporative cooling. The drying flow rate was varied, but first it was necessary to determine whether the drying rate itself affected the permeation rate through convective heat transfer.
9.5.1 Effect of Drying Flow Rate on Permeation Rate with Sample Dry

Figure 121 shows a portion of Trial i59. At 127 minutes, the drying rate was changed from 200 to 100 mL min\(^{-1}\). At this stage the sample had little or no surface solvent left, so changes in the drying flow rate would relate directly to convective heat transfer to the sample by the drying flow itself, not evaporative changes enhanced by the drying flow. There was no change in the permeation rate that could be attributed to the change in drying flow.

![Figure 121 Effect of drying flow rate on permeation rate, Trial i59](image)

The "glitch" shown in Figure 121 at the end of the wet time and beginning of the dry time caused by a reduction in the permeation rate by evaporative cooling was noted in Chapter 9 and is now further investigated. The expected trajectory of the permeation curve in the absence of the "glitch" is shown with a dashed line.

9.5.2 Effect of Drying Flow Rate on Permeation Rate with Sample Wet

A cycle time of 2 minutes and wet time of 1 minute was chosen for Trial i1708 (Figure 122) with acetone and reference neoprene, to maximise the effect of cooling attributed to the drying flow and produce a row of the "glitches".
A drying flow rate of 226 mL min\(^{-1}\) for the first 70 minutes permitted the system to approach equilibrium. The drying flow rate was then decreased to 120 mL min\(^{-1}\) for 9 minutes, followed by an increase to 556 mL min\(^{-1}\). The drying flow values of zero during the wet time have been excised for clarity.

The experiment was repeated with a wider range of drying flow rates from 66 mL min\(^{-1}\) to 4000 mL min\(^{-1}\). At 4000 mL min\(^{-1}\), the permeation rate increased slightly, possibly due to bulging and thinning of the sample.
Qualitatively, the drying flow rate made no difference to the permeation rate or the cyclic dips in the permeation rate. Correlating the drying flow rate with the permeation rate (Figure 123) shows that 2.6% of the variation in permeation rate can be attributed to variations in the drying flow rate.

![Figure 123 Correlation of drying flow rate with permeation rate](image)

The permeation rate was affected by the drying flow apparently due to evaporative cooling, but it was insensitive to fluctuations in the drying flow rate. However, at very low flow rates, where conditions are stagnant, increases in the drying flow rate would be expected to produce a significant increases in evaporative cooling. Saturated vapour collecting at the sample would be removed with increasing efficiency as the drying flow rate increased, increasing the rate of evaporation. Above a certain rate, the evaporative cooling would become unrealistically high to represent the workplace. This point was not determined.

Under stagnant condition, drying of the sample would be slow and the wet time would be poorly defined, so stagnant conditions were not investigated.

### 9.5.3 Correlation between Sample Surface Temperature and Permeation Rate

The data in Figure 122 from Trial i1708 are replotted in Figure 124 to try to discover any relationship between the permeation rates and the surface temperatures. There are patterns, but they are complex as the permeation rate not only changes cyclically, but
the height of the peaks varies. The plot may suggest a collection of overlaid lines, like the ones apparent at low permeation rates.

Figure 124 Plot of permeation rate against ample surface temperatures, trial iAug17

The derivative of the data from 40 minutes onwards in Figure 124 is replotted in Figure 125 to reveal distinct relationships between rates of changes in the sample surface temperature and permeation rate. The upper plot in Figure 125 shows the rate of change of permeation rate against rate of change of the temperature on the wet side of the sample from 40 minutes onwards. This presentation effectively normalises the data and emphasises any patterns in the changes. The lower plot shows the same for the dry side of the sample.
Under near steady cyclic permeation conditions, 80% of the change in permeation rate ("glitch") was explained by the temperature of the wet side, but the rate of change on the dry side was much slower and correlated less well ($r^2 = 69\%$). A more elaborate fit than a simple linear regression may produce between fits as the Rate of change of permeation rate levels off with positive rates of change in temperature. The difference between the wet and dry side may be attributed to the CPC sample insulating evaporative cooling on the wet side from the dry side. The evaporative temperature change appears to account for the "glitch".

Figure 125 Rates of change of permeation rate and temperature, Trial i1708
SECTION 9.6  EFFECT OF CYCLE TIME ON PERMEATION

9.6.1  Cycle Time Experiment
The *GloveTest* code was modified to permit an automatic increment of the cycle time every ten cycles whilst keeping the wet time constant at one minute, so as to reveal the changing pattern of permeation with cycle time in a single trial. The temperature of the collecting gas remained unchanged into and out of the cell, and the collecting flow rate remained within 1% of the set rate (600 mL min\(^{-1}\)) throughout the experiment. A bug in the code halted the experiment at midnight, limiting the maximum cycle time to 9 minutes. Over 23,500 sets of data were collected to this point.

9.6.2  Results of Cycle Time Experiment
In Figure 126 the time and permeation rate scales vary, to place emphasis on the changing shape of the permeation rate pattern. The last three cycles in each set are shown. The smaller curves at the bottom of the plots are the temperatures of the dry and wet side and an indicator of the wet or dry part of the cycle.
Figure 126 Effect of cycle time on permeation rate and pattern, Trial i74

Chapter 9. Effects of Operational Parameters on Cyclic Intermittent Exposure 229
When the cycle time was three minutes (CT 3), the permeation rate in the wet time was affected by warming of the sample by the acetone. In the dry time, it was affected by evaporative cooling of the acetone, although the average permeation rate was determined by the cycle time. Near isothermal conditions existed in the sample only during the wet time, as shown by the convergence of the curves for "T wet" and "T dry" during the wet part of the cycle.

The increment to a cycle time of 4 minutes showed a slight change in the pattern, with other unidentified mechanisms increasing permeation in the second half of the dry time. Convective warming from the collecting flow and drying flow was suspected, though an increase in surface temperature was not measured. As the thermocouples were on the two surfaces of the sample, they would be indicative of both the surface temperature of the sample and the temperature of the nitrogen flows. There was always some uncertainty as to what temperature was measured. It was possible that surface warming had begun despite recorded temperatures not showing this, due to the thermal inertia of the thermocouples and the fact that only one side of the thermocouple junctions on the sample was in contact with the sample. When the sample was wetted with acetone, conductive warming of the sample predominated.

The change to a cycle time of six minutes revealed something of the underlying permeation process with an apparent steady state permeation rate at "A", just before the end of the dry time. Here, the temperature gradient across the sample was about 10°C, but steady. With the subsequent wet time, isothermal conditions some ten degrees warmer (20°C) occurred. This pattern continued through to a cycle time of 9 minutes.

A permeation rate that was representative of the permeation under isothermal conditions would have to be selected at the solid square rather than the solid circle (as shown on the CT 9 plot in Figure 126), though for most of the cycle a near constant temperature gradient occurred across the sample. The trend of isothermal permeation rates is shown in Figure 127 for Trial i74 which was run over 12 hours with automatic incrementing of cycle length. The data for cycle length 2, 3 and 4 minutes were discarded, as steady state cyclic conditions were not established for these values. However, extrapolation to a cycle length of zero gave a permeation rate of 217 μg cm⁻²min⁻¹ that concurs with the SSPR for continuous exposure.
When the cycle length was increased closer to 15 minutes (Figure 128), the permeation rate during the dry time may even briefly exceed the permeation rate during the beginning of the wet time. At the beginning of the wet time, the temperature of the sample took time to return to the "experiment temperature" for permeation to proceed at this higher temperature. In addition, the solvent entering the sample during a wet time taking a finite time to diffuse through the sample. The solvent peak is apparent about four minutes into the dry time, but greatly affected by the evaporative cooling.
Measurements with long cycle times were not performed in Trial i74 (as the software timers reset at midnight), but the effects of small amounts of solvent in the polymer matrix would still be expected to have an effect on permeation. This was observed in the previous chapter with Trial i60 in comparing the data from a sample exposed to acetone vapour with the ASTM F1383-1996 data. The small amount of solvent in the neoprene increased the permeation through the neoprene some 15 minutes later. This topic will be further explored in the next chapter, where modelling removes some of the resource constraints inherent in experimental work.

9.6.3 Temperatures Variation during Cycle Time Experiment

The room and nitrogen temperatures were both 21±1°C for most trials, but the temperatures of the sample within the cell varied much more. The data for Trial i74 were for 12 hours and typifies the temperature ranges measured, though smaller temperature drops in the collecting gas were sometimes found. (Some of the data was culled from the trial, as a software error permitted the cell to remain in drain mode at the end of each sequence of 10 cycles for a given cycle time. This permitted analysis of the data under conditions of regular cyclic intermittent exposure, with cycle times changing after ten cycles.)

The data set of drying nitrogen cell inlet and outlet temperatures and the wet and dry surface temperatures of the neoprene are shown in Figure 129. The air-conditioning in
the laboratory appears to have failed around midnight, so the summary data in Table 22 excludes the last set of data for CT 9 minutes.

The temperatures in Figure 129 were generally ranked Inlet - Outlet - Dry - Wet and the extremes and averages are summarised in Table 22.

![Figure 129 Intermittent cell temperatures, trial i74](image)

Table 22 Temperatures during Trial i74

<table>
<thead>
<tr>
<th>Collecting flow of nitrogen (°C)</th>
<th>Sample temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T inlet</td>
<td>T outlet</td>
</tr>
<tr>
<td>Maximum</td>
<td>21.4</td>
</tr>
<tr>
<td>Minimum</td>
<td>19.7</td>
</tr>
<tr>
<td>Average</td>
<td>20.5</td>
</tr>
</tbody>
</table>

Table 22 shows the inlet and outlet temperatures to be relatively stable, generally within 1°C. The collecting flow outlet temperature varied less than the inlet temperature, but was on an average, 0.7°C colder. The large differences were between the Wet and Dry sides of the sample, with a maximum difference of 9.1°C, some what less than the 19.7 to 6.4°C (13.3°C) range in temperature of the wet side due to evaporative cooling, as shown in Table 22. The dry side slowly follows the temperature of the wet side. What Table 22 does show is the need to measure the temperature of the sample, not the relatively stable collecting gas temperatures. If a single experiment temperature was to be used, then it is not obvious what temperature should be considered. An average of
wet and dry sample surface temperatures may be the most representative temperature, giving an estimate of the temperature at the centre of the sample. This

The variation in the temperature of the nitrogen collecting gas into the cell may be due to temperature changes in the long line between the gas bottle and the cell. The gas to the experiment flowed from bottles on the outside of the building, inside the building for thirty metres, and then through another six metres of 6-mm pneumatic tubing before entering the experiment. The average inlet temperature of the gas was 21.4°C, but varied ± 2°C over the 12-hour experiment. Most of this difference occurred in the last 30 minutes, near midnight, when air conditioning capacity may have been reduced, limiting regulation of room temperature. For most of the experiment, the temperature was regulated to within 1°C.

When the temperature in an experiment is required to be reported, such as in ASTM F739-1996 and ASTM F1383-1996, the location of the measurement and the type of temperature sensor will make a difference to the reported temperature. The room temperature and temperature of the collecting gas flows into and from the cell were usually within 1° of 21°C. Immersing the cell in a water bath or a GC oven would regulate the cell temperature, but have little effect on the temperature of the sample during intermittent exposure.

SECTION 9.7 CONCLUSIONS

9.7.1 Effect of Directing Drying Flow Direction on Flow Pattern
The dye studies on the drying flow patterns revealed that the offset inlet port for the drying gas produced a swirling flow which appeared to be close to optimum. It produced a vigorous flow next to the test sample that would efficiently remove residual solvent. This flow also resulted in a clearance of dye from the wet side of the cell in 4 seconds, half the time that it took with the drying flow directed across the cell.

The addition of a nozzle to the inlet port for the drying flow did not significantly enhance the swirling pattern near the sample. The most noticeable effect of the nozzle occurred when the flow was directed away from the test sample, resulting in the region next to the sample becoming stagnant.
9.7.2 Effect of Drying Flow Rate on Permeation Rate

The drying flow rate, in itself, had little effect on the permeation rate when the sample was dry. Similarly, when the sample was wet, the drying flow rate had little effect on the permeation rate or the cyclic dips in the permeation rate over a range of 120 mL min\(^{-1}\) to 556 mL min\(^{-1}\). At 4000 mL min\(^{-1}\), the permeation rate increased slightly, possibly due to stretching of the sample. There is a need for additional trials with other less volatile solvents to determine the effect of the drying flow rate on permeation rate, as less volatile solvents may not evaporate as quickly as acetone.

Further studies are required with solvents less volatile than acetone to fully evaluate the effect of drying flow rate on permeation rates. Evaluation over a greater range of drying flow rates, particularly low (< 50 mL min\(^{-1}\)) would also be desirable.

9.7.3 Effect of Sample Temperature on Permeation Rate

When the cycle time was short so that the permeation rate was highly affected by evaporative cooling, the rate of change of temperature of the wet side explained 80% of the permeation rate fluctuations, but only 69% on the dry side. The direct effect of temperature on permeation rate was less clear, as the peaks in the cyclic permeation tended to vary in height.

This effect may be different for less volatile solvents, but the same general pattern would be expected.

9.7.4 Effect of Cycle Time on Permeation Rate

When the cycle times were short, up to 9 minutes, the evaporative cooling associated with removal of the acetone from the neoprene caused a reduction in the permeation rate and a temperature gradient of 10°C across the sample. This was disrupted by the next wet time with a return to isothermal conditions and an increase in the permeation rate. Longer cycle times produced more complex patterns involving static temperature gradients and increases in permeation by other undetermined mechanisms.

The underlying isothermal permeation rate for a fixed wet time was an inverse linear function of the cycle time with an extrapolated permeation rate of 217 µg cm\(^{-2}\)min\(^{-1}\) at zero cycle time. This was close to the measured continuous exposure SSPR for acetone-reference neoprene of 201.9±7.5 µg/cm\(^{2}\)/min in Table 4.
For less volatile solvents, the evaporation rate would be less so the evaporative cooling would be less. The degree of the change would be expected to be different for less volatile solvents, through the same general patterns would be expected to be similar.

9.7.5 Measurement of Experiment Temperature

When the temperature in an experiment is required to be reported, such as in ASTM F739-1996 and ASTM F1383-1996, the location of the measurement and the type of temperature sensor will make a difference to the reported temperature. Immersing the cell in a water bath or a GC oven would regulate the cell temperature but have little effect on the temperature of the sample during intermittent exposure. As the drying flow rate was not specified in ASTM F1383-1996, it would be difficult to replicate permeation rates in different laboratories.
CHAPTER 10. MODELLING INTERMITTENT EXPOSURE

SECTION 10.1 AIM

There are no known prior attempts to model intermittent exposure of CPC. The aims of this chapter are to

- develop an appropriate mathematical solution to the model for permeation of CPC under conditions of intermittent exposure;
- compare the solution with experimental data and investigate the properties of the solution; and
- investigate whether there are permeation indices specific to intermittent exposure that could be applicable in the workplace.

SECTION 10.2 INTRODUCTION

The analytic solutions for permeation rate (PR) and cumulative permeation (CP) used in Chapter 6 for continuous exposure are not suitable for application to intermittent exposure as they do not describe the complex concentration gradients that develop through the thickness of a CPC sample under conditions of intermittent exposure.

An analytic solution using Fourier Analysis was considered, to simulate intermittent exposure by having changing boundary conditions that approximated intermittent exposure. However, this model may not have had analytic solutions if further complexities such as temperature gradients or varying diffusion coefficients were introduced.

Instead, a numeric approach was implemented, solving the partial differential equations for Fick's Second Law numerically and then varying the boundary conditions with time to simulate intermittent exposure. This approach made it straightforward to produce more complex boundary conditions, which simulate random intermittent exposure and concentration dependent diffusion. Both are investigated in this chapter.

10.2.1 Numeric Solutions to Intermittent Model of Permeation

Three numeric solutions of increasing complexity were outlined in Crank (1975) and all were implemented to simulate the permeation of chemicals through CPC under intermittent exposure. They relied on calculations at predetermined time intervals to estimate the changing concentration profile through the thickness of the CPC, divided into ten or more "layers". Figure 130 shows how the values in one cell, representing a
layer at a point in time, affect the concentrations in adjoining layers and at subsequent times. Three solutions with increasing complexity are shown.

![Diagram showing numeric solutions for modelling intermittent exposure]

Figure 130 Numeric solutions for modelling intermittent exposure

The "Simple" solution gave the new concentration in a layer by averaging the concentrations in the adjoining layers. This approach was easy to construct with elementary spreadsheet instructions, copying the formula to average the value of the concentration in the “adjoining layers” across a row representing the next time increment. No special coding was needed.

The "Explicit" solution used a weighted average of the three adjoining layers to give the new value in the middle layer. This required simple construction of a formula to give the desired calculation, and to copy the formula across a row representing the next time increment.

For the "Implicit" solution, the concentrations in adjoining layers in the new time increment were also used in the calculations. This demanded simultaneous calculation of the concentrations in a new layer. This was somewhat more complex, and it was solved using the Visual Basic for Applications macro language available with Microsoft Word’97. Matrix commands simplified the arithmetic.

For each of these solutions, a spreadsheet matrix was constructed to represent the CPC sample with the left and right columns representing the chemical concentrations on the two surfaces of the CPC. For intermittent exposure with an initial zero concentration through the thickness of the CPC, one surface had a changing concentration and the other was kept at zero. The columns between represented the changing concentration profile in each layer with time. Each row represented a time increment that depended on the concentration profile in the previous row.
Continuous exposure was used as a special case of intermittent exposure, as continuous exposure could be thought of a series of adjoining intermittent exposures. This gave at least one check of the numeric solutions for intermittent exposure against an established analytic solution for continuous exposure.

The boundary conditions for intermittent exposure for a membrane thickness $L$ and initially dry were:

Initial, $t = 0$, $C(0, 0) = 0$, $C(L, 0) = 0$

Time $T$, $t = T$ $C(0, T) = C(t)$, $C(L, t) = 0$

where $C(t) = C$ for $t = t$ modulo cycle time to $t +$ wet time

= 0 otherwise

By using the “modulo” function, the time axis was easily divided into cycles of the desired length.

**SECTION 10.3 STANDARD CONDITIONS**

The Standard Conditions developed in Chapter 6 for continuous exposure of CPC were further expanded for intermittent exposure to give realistic reference values for the numerical solutions to the model.

**Table 23 "Standard Conditions" for the Intermittent model**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPC thickness</td>
<td>0.05 cm</td>
<td>Used by Schwope et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>0.04 cm</td>
<td>Reference neoprene from ASTM F739 (1996)</td>
</tr>
<tr>
<td>Dry concentration</td>
<td>0 $\mu g$ cm$^{-3}$</td>
<td>Assumed instant removal of permeant</td>
</tr>
<tr>
<td>Wet concentration</td>
<td>10,000 $\mu g$ cm$^{-3}$</td>
<td>Any large number would suffice. Used where comparison with the data from Schwope et al. (1988) was not an issue</td>
</tr>
<tr>
<td>Solubility</td>
<td>$4.9 \times 10^4$ $\mu g$ cm$^{-3}$</td>
<td>Used by Schwope et al. (1988)</td>
</tr>
<tr>
<td>Initial concentration</td>
<td>0 $\mu g$ cm$^{-3}$</td>
<td>Assumed no chemical in CPC matrix at start</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$2.5 \times 10^{-6}$ cm$^2$ min$^{-1}$</td>
<td>Used by Schwope et al. (1988)</td>
</tr>
<tr>
<td>Cycle time</td>
<td>15 or 150 minutes</td>
<td>ASTM F1386 (1996) used 15 minutes, but for lower values of D, 150 minutes permitted the oscillatory intermittent pattern to develop.</td>
</tr>
<tr>
<td>Wet time</td>
<td>1 or 10 minutes</td>
<td>ASTM F1386 (1996) used 1 min, but 10 min gave the same wet-dry ratio when a cycle time of 150 minutes was used.</td>
</tr>
<tr>
<td>Collecting volume</td>
<td>100 mL</td>
<td>For closed loop permeation, used by Schwope et al. (1988)</td>
</tr>
</tbody>
</table>

Where appropriate, these Standard Condition values were used.
SECTION 10.4 IMPLEMENTATION OF NUMERIC SOLUTION TO MODEL

Further details of the spreadsheet implementation of the Simple and Explicit solutions are given in Appendix G as they were both discarded in favour of the Crank-Nicolson Implicit solution.

10.4.1 Crank-Nicolson Implicit Method

The solution given by Crank (1975) was implemented using Excel'97 spreadsheets using formula written with Visual Basic for Applications (VBA) and the spreadsheet's matrix inversion (MINVERSE) and matrix multiplication (MMULT) functions. The solution was reputed to be stable for all values of a time scaling factor \( r \) used in Equation 25.

**Implicit method theory**

According to Crank (1975), the finite difference representation of the slice "i" and time "j" is given by

\[
\frac{c_{i,j+1} - c_{i,j}}{\delta T} = \frac{1}{2} \left\{ c_{i+1,j} - 2c_{i,j} + c_{i-1,j} + c_{i,j+1} - 2c_{i,j} + c_{i,j-1} \right\} + O\left(\delta T\right)^2 + (\delta X)^2 \}
\]

..................Equation 24 Crank's solution to flux

where

- \( c_{i,j} \) the concentration in the \( i^{th} \) layer at time \( j \)
- \( \delta X \) the thickness of each "layer"
- \( \delta T \) the time increment between calculations
- \( O\left(\delta T\right)^2 + (\delta X)^2 \} \) the total error

To translate this into a form suitable for formulation as a spreadsheet, the elements became

\[
-rc_{i-1,j+1} + \left(2 + 2r\right)c_{i,j} - rc_{i+1,j+1} = rc_{i-1,j} + \left(2 + 2r\right)c_{i,j} + rc_{i+1,j}
\]

..................Equation 25 Spreadsheet flux formula

where \( r = \frac{\delta T}{(\delta X)^2} \)

Equation 25 was solved by calculating the matrix equation

\[
A \cdot C_{i,j+1} = v + B \cdot C_{i,j}
\]

..................Equation 26 Matrix solution for flux
where

\[ C_{i,j+1} \] vectors for concentrations \( c_{i,j} \) at time \( j+1 \)

\[ C_{i,j} \] vectors for concentrations \( c_{i,j} \) at time \( j \)

\( v \) vector \( \{ f_{\text{wet}}(t_j), 0, 0, ..., 0, f_{\text{dry}}(t_j) \} \), describing the boundary conditions

\( A \) matrix of the coefficients on the left side and

\( B \) matrix of the coefficients on the right side.

Inverting \( A \) (i.e. \( A^{-1} \)), and rearranging gives

\[
C_{i,j+1} = A^{-1} v + (A^{-1}B)C_{i,j}
\]

...............Equation 27 Rearranged matrix solution

Thus, the new concentrations \( C_{i,j+1} \) may be calculated directly from the old concentrations, \( C_{i,j} \).

SECTION 10.5 COMPARISON OF NUMERIC INTERMITTENT SOLUTIONS

The three numeric intermittent solutions, simple, explicit and implicit, were compared in order to reveal their differences. The numeric solutions were first compared with the analytic solution, for continuous exposure.

10.5.1 Continuous Exposure

Under Standard Conditions and continuous exposure, the numeric solutions all agreed with the analytic permeation rate solution as the plots are almost identical and are indistinguishable in Figure 131. The horizontal line at the bottom of the plot indicates continuous wetting of the sample.
Chapter 10. Modelling Intermittent Exposure

This demonstration of congruence between the analytic and numeric solutions was essential as it demonstrated that for at least continuous exposure, the continuous analytic solution and the numeric intermittent solutions were equally valid.

### 10.5.2 Intermittent Exposure

When cyclic intermittent exposure was introduced, with one minute of wet in each two-minute cycle, the permeation rate halved. The three numeric solution curves were essentially the same, with the Explicit solution diverging due to slight instabilities in calculation of wet times.
Chapter 10. Modelling Intermittent Exposure

The prediction of 50% permeation rate with 50% wet time gave further credence to the intermittent models. When the cycle time was increased to 15 minutes, the solutions noticeably diverged (Figure 133).

Figure 132 Numeric solutions, intermittent exposure, wet 50% of cycle

The Simple solution and the Explicit solution gave comparable results, but the Implicit solution gave a much more gradual growth in the first 45 minutes. This was because the values in the cells that propagated forward with each time slice in the Simple and

Figure 133 Comparison of numeric solutions for intermittent exposure

The Simple solution and the Explicit solution gave comparable results, but the Implicit solution gave a much more gradual growth in the first 45 minutes. This was because the values in the cells that propagated forward with each time slice in the Simple and
Explicit solutions were unaware of changing concentrations behind them. In contrast, the Implicit solution was fully calculated through all layers of the sample for every time slice. It was therefore thought that the Implicit solution more accurately portrayed the permeation process.

SECTION 10.6 VALIDATION OF NUMERIC SOLUTIONS TO INTERMITTENT MODEL

10.6.1 Validation against Published Calculated Data
The Implicit solution was compared with Table 8.3 in Crank (1975) which presented a check of his numeric solution against an analytic solution. Identical numbers were produced (to the 4 significant figures published) demonstrating that the implementation of the model for this work was not basically flawed. Details are given in Appendix G. These values could only check the model under conditions of continuous exposure.

10.6.2 Validation against Analytic Solutions
The Implicit solution was used to calculate a trial of 508 minutes under Standard Conditions with continuous exposure and \( r = 0.3125 \). (The value of \( r \) was arbitrary, but permitted a large number of points to be calculated within the column limits of the spreadsheet.) This permitted steady state conditions to be established half way through the trial. The Permeation Rate and Cumulative Permeation (trapezoidal integral of Permeation Rate) at the end of the trial were compared with the corresponding figures from the analytic solutions to give the worst estimate of the errors in Table 24.

<table>
<thead>
<tr>
<th>% difference in PR</th>
<th>% difference in CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0003</td>
<td>-0.26</td>
</tr>
</tbody>
</table>

The plots of the permeation rate and cumulative permeation data from the two approaches were indistinguishable by eye. The calculated errors were acceptable and much smaller than experimental errors for measured data. The Explicit solution code was also validated against the analytic solutions with similar errors.

10.6.3 Comparison with Published Experimental Data
The only published intermittent exposure data were those in Figure 5 of ASTM F1383-1996, to illustrate the form of the permeation curve. To apply the Implicit solution to fit this data, the CPC thickness was set to 0.04 cm (400 \( \mu \)m), the thickness of the reference neoprene. The cycle time was set at 15 minutes and the wet time at 1 minute. Fits of the
Implicit numeric solution to the ASTM F1383-1996 data are shown in Figure 134 for three different values of D, with the wet concentration (S/l) adjusted to scale the plots. This scaling permitted the shape of the permeation curve to visually overlay the published ASTM F1383-1996 data.

Figure 134 Implicit solution and ASTM F1383-1996 intermittent data

The ASTM data are shown as a line with filled circles indicating measured values.

- **Curve "A"** attempts to fit the timing of the peaks of the implicit solution to the ASTM data, but produces a poor fit for the first two cycles.
- **Curve "B"** has a higher value of D and attempts to fit the magnitude of the oscillations to the ASTM data.
- **Curve "C"** attempts to model the data in the first cycles, but underestimates the permeation in subsequent cycles.

No single curve properly describes the ASTM F1383-1996 data.

A good fit to the ASTM F1383-1996 data was obtained with a sample pre-exposed to acetone vapour from Chapter 9, so it appears that some alteration to the permeation process before a trial can result in a replicable experimental curve. However, the poor fit of the Implicit solution to the same ASTM F1383-1996 data suggests either that the solution was inappropriate, or that some factor that varied with concentration or time retarded the permeation process. This was also observed in Chapter 6 with the Griffith cell validation data where the solution increased faster than the experimental data. It
was suspected a better fit required a diffusion coefficient that varied with solvent concentration in the polymer. The permeation process in the reference neoprene is complex as the effects of swelling of the polymer would not simply reverse during drying of the polymer between exposures.

**Position of peaks in intermittent cycle**

The peaks in an intermittent exposure permeation curve are an obvious feature of the curve, but the shape and phase of the peaks had not been investigated. By plotting the time, modulo\(^7\) the cycle time, it can be seen that at least the first peak in the Implicit solution can be expected to be at a different point in the cycle to the other peaks. An example is plotted in Figure 135 with a cycle time of 60 minutes with \(D = 4 \times 10^{-6} \text{ cm}^2\text{min}^{-1}\). Here, a longer cycle time than the standard 15 minutes was chosen, but with a smaller diffusion coefficient. This resulted in similar shaped curves to those calculated from Standard Conditions.

---

\(^7\) The mathematical “modulo” function permitted easy calculation of each cycle for cyclic intermittent exposure. The time into each cycle was simply “\(t \mod CT\)”, where \(t\) is the time and \(CT\) is the cycle time. Each cycle started with a wet-time and the remainder of the cycle was the dry-time. Care had to be taken in the calculation, as the number of time slices could be affected by rounding errors in the calculation of the cycle times.
A similar pattern is apparent in the ASTM F1383-1996 data for a cycle time of 15 minutes in Figure 136.

The choice of a cycle time of 15 minutes for the ASTM data allows the peaks to be present just before the next cycle starts. At the beginning of the new cycle, the permeation rate has just begun to drop. This choice of cycle time may have obscured
any reduction of permeation related to cooling of the sample from the evaporation of the acetone.

The reason for the shift in peaks in both the Implicit solution and the ASTM data might be explained by the fact that the first peak starts from a zero or near zero permeation rate, whereas the subsequent peaks start from a non zero value. The effect would be reduced in longer cycles when the permeation rate was close to zero at the end of a cycle.

**SECTION 10.7 IMPLICIT SOLUTION EXPERIMENTS**

A number of trials were performed to investigate the effect of changing parameters and to examine features of the Implicit solution.

**10.7.1 Effect of Cycle Time on Pattern of Permeation**

The cycle time could be expected to affect not only the peak values of the permeation curve but the shape of the permeation curve.

The Implicit solution with Standard Conditions was used to calculate the curves for different cycle times. Similar results were obtained with the Explicit solution. The analytic solutions were also plotted for continuous exposure, and in Figure 137 (left plot), the two curves were coincident.

![Figure 137 Implicit solution, continuous and 50% exposure](image)

The Permeation Rate and Cumulative Permeation both dropped by half (50.00%, 49.92%), but the curves appeared smooth, without visible oscillations from the intermittent exposures. The decrease was perhaps intuitive, as the total chemical contact time to the CPC had been halved. When the cycle time was increased to 50 minutes in Figure 138, the drop was almost 80%, and some periodicity was evident. The plots are...
shown without the analytic solution curve for continuous exposure, to highlight the periodicity in the curve.

![Permeation curves with cycle time](image)

**Figure 138 Development of permeation curves with cycle time**

On increasing the cycle length to 100 minutes, a more pronounced periodicity was evident. Doubling the time again to 200 minutes, the trend of increasing periodicity continued. When the cycle time was increased to 300 minutes, the peaks were noticeably asymmetric. At a cycle time of 480 minutes (8 hours) in Figure 139, the time scale on the left plot was lengthened to show three peaks, to demonstrate that the pattern repeated itself after the first peak.

![Permeation curves with cycle time](image)

**Figure 139 Cycle time 480 minutes, wet time 10 minutes**
The peak asymmetry was very pronounced for this cycle time. The permeation rate had almost returned to zero at the end of the first cycle, but it still had a significant effect on the next peak as some solvent “remained” in the polymer. On the right, the permeation curve was replotted with the Analytic solution curve for continuous exposure to emphasise the drop in peak permeation rate as the cycle time increased.

Further increases in length of cycle had little influence on the peak permeation rate.

The pattern for a cycle time of 600 minutes on a normalised scale as before and compared with continuous exposure in Figure 139 shows how the maximum permeation rate has dropped as cycle time increases. This drop is not as evident as in Figure 138.

10.7.2 Effect of Cycle Time on Peak Permeation Rates.
The peak permeation rate estimate could be of significance when the wearing period is short and the acute health effects are related to the concentration of a chemical. This may occur with some skin irritants where a threshold is apparent or for chemicals that are quickly metabolised, excreted or otherwise removed. Biotransformation of chemicals may occur in the skin (Emmett, 1991), or the chemical may be locally removed by blood flow near the surface of the skin, sweat and ventilation of the CPC. These mechanisms would limit cumulative exposure of the chemical to the skin and make the effects of peak permeation rates more important.

As expected, the peak permeation rate decreased as the cycle time increased, as shown in Figure 140. However, it was not possible to determine whether a simple reciprocal relationship exists between cycle times and peak permeation rates by presentation of the data in this form.
The nature of the relationship is more evident with cycle frequency, defined here as the reciprocal of cycle time, in Figure 141. To emphasise a deviation from a simple reciprocal relationship at long cycle times (low cycle frequencies); the scale is truncated at a cycle frequency of 0.1 min$^{-1}$. At long cycle times the peak permeation rate asymptotes to a constant, indicating that each peak is independent and identical to the first peak. If the peaks are close to each other (high cycle frequencies), then simple reciprocity of peak permeation rate and cycle time occurs.

**Figure 140 Effect of cycle time on peak permeation rate**

**Figure 141 Effect of cycle frequency on peak permeation rate**
A linear least squares fit for a cycle frequency > 0.05 (cycle time < 20 minutes), was very good ($r^2 = 0.999987$) but for cycle times greater than this, the linearity slowly vanished. This was because the CPC was effectively dry, well before the next exposure and the peak permeation rate for these isolated peaks is the same as for the first peak.

### 10.7.3 Effect of Cycle Time on Cumulative Permeation

For many chemicals, the toxic effects would be related to the cumulative exposure rather than the peak concentration. This particularly applies for chemicals that are more slowly metabolised or excreted and build up in the body to exert their toxic potential.

By numerically integrating the area under the intermittent permeation curves for different cycle times, the cumulative permeation at different times may be estimated.

The effect of cycle time on cumulative permeation is plotted in Figure 142 for different cycle times. The cumulative permeation was little affected by the cycle time until breakthrough was evident at about 5 minutes.

![Figure 142 Effect of cycle time on cumulative permeation](image)

There were two asymptotes for cumulative permeation in Figure 142, given by continuous exposure as an upper limit, and a single initial one-minute exposure given by the 90-minute cycle time curve, as the lower limit. For increasingly shorter cycles, cumulative permeation asymptotes to the continuous exposure curve, and the effects of individual wet periods were less obvious.
In assessing the effects of cycle time on cumulative permeation cycle times of the same order as the experiment time can give unusual results. In Figure 142, cumulative permeation at 90 minutes (experiment time) for cycle times of 30, 60 and 90 minutes illustrate this. Though the cycle time of 60 minutes would suggest half the cumulative permeation for 30 minutes, this is clearly not so. A peak that is just included in the integration (60 minutes) will give a greater cumulative permeation than one that just missed the 90 minute point (90 minute cycle time). For this reason, only cycle times that are much shorter than the exposure time will be considered.

A plot of the cumulative permeation against cycle time gave a similar curve to Figure 140 for peak permeation rate. However, when plotted against cycle frequency (Figure 143), the plot was linear ($r^2 = 0.9999986$), despite the complexities of the permeation curves.

![Figure 143 Effect of Cycle Frequency on cumulative permeation](image)

It was not obvious that cumulative permeation (for cycle times much less than the exposure time) would follow a simple reciprocal relationship with cycle time, but that peak permeation rates would not. The recommendation in ASTM F1383-1996 to use cumulative permeation as an index of permeation for intermittent exposure appears to have validity, but the additional use of peak permeation rates may have a toxicological basis. However, these calculations were performed for regular cyclic exposures and the effect of random exposures will now be considered.
10.7.4 Random Intermittent Exposure

There are a number of ways to emulate the more random exposures that would be expected in a workplace. Even cyclic tasks will have some variation of times between cycles. Truly random exposures could easily be modelled, but it was decided to model exposure patterns that had the same mean cycle time between exposures to permit a comparison with regular cyclic exposures. Two simple approaches were considered, each cycle starting with a one minute wet time and either

1. varying cycle times randomly about a mean cycle time or,
2. randomly choosing cycle times within a given range.

The first approach would produce a Gaussian distribution of these cycle times about the mean cycle time and may be appropriate if the exposures were close to regular. The cycle time distribution would be characterised by the mean cycle time and its standard deviation. The obvious limitation would be that negative cycle times would not be permitted (the next cycle beginning before the present cycle ends).

The second approach was chosen, using a random cycle time between zero and twice the cycle time, with equal probabilities for any cycle time in this range. This gave a greater probability of two cycles following each other and better emphasised the effect of random cycle times on permeation rate. The distribution of cycle times would approximate to a truncated Gaussian distribution with a large standard deviation.

Computer code for random exposures

Additional computer code was developed for the Implicit solution to calculate random wet cycles. This is given in Appendix G. This code enabled the effects of random cycles on peak permeation rates and cumulative permeation to be estimated. The times at wet values were calculated with this code. The permeation values were then automatically calculated and plotted. A "check-box" option to calculate "regular" cycles was included in the code to allow comparisons of random and regular cycles.
Some of the higher cumulative permeations calculated would have been due to extra cycles and the lower cumulative permeation's due to random fewer exposures. The experiment was run for 120 minutes with a range of cycle times from 0 to 30 minutes to give a mean cycle time of 15 minutes.

Results of random exposure experiment

Figure 144 shows a typical random intermittent exposure permeation curve.

![Permeation Rate Graph](image)

**Figure 144 Random exposure permeation rate**

Repeating the experiment and comparing the results against the pattern for regular intermittent exposures (darker line in Figure 145) showed the effect of random exposures and the effect on peak permeation rates.
For truly random exposures, there would be a small probability that all exposures directly followed each other, emulating continuous exposure. Thus, the continuous exposure permeation curve gave the extreme upper limit for random intermittent exposure. It is evident in Figure 146 that this was unlikely to occur.

The most useful feature of the solution was a determination of the likely effect on cumulative permeation. The averaging effect of successive random exposures tends to cancel and a near straight line occurs. It can be seen in Figure 147 that sometimes the
cumulative permeation is smaller and sometimes it is larger than the regular, cyclic intermittent exposure cumulative permeation.

The variation in cumulative permeation averaged an 8% increase, with a maximum of 31% increase, much less than the variation in peak permeation rate (up to 84% increase), due to the averaging effects of cumulative exposures.

If acute affects like skin irritation are related to peak levels, then random patterns of exposure could significantly affect the peak levels and thence the concentration inside the CPC. A conservative estimate of the peak levels, perhaps by a factor of two or more, would be required if the intermittent exposures were not regularly spaced. The variation in cumulative permeation would be less than for peak permeation, and would probably be less than the uncertainty in the published or measured permeation data for continuous exposure.

10.7.5 Numeric Solutions of Intermittent Exposure vs Experimental Data

Implicit solution vs experimental acetone-reference neoprene data
Experimental data from intermittent exposure of reference neoprene (thickness 400 μm, and using the Griffith Intermittent Mk2 cell) with the same exposure regime as the Implicit solution (15 minute cycle with 1 minute of wetting) is shown in Figure 148.
Superficially, the curves look similar, but the following differences are noted:

- the first peak in the experimental data does not occur in the first cycle of the model,
- early permeation rates are very different – earlier permeation occurred with the model,
- a different phase- the calculated data equilibrates more quickly after a Wet time, and
- the depth of the oscillation is less for the calculated data

Measurements of the temperature of the exposed and drying surfaces of the reference neoprene during testing indicated a significant (12°C) temperature change and complex pattern. This would affect both the D and S and may account for much of the peak to peak swing.

Changing the model parameters to a smaller diffusion coefficient and applying the appropriate scaling gave Figure 149.
Figure 149 Implicit solution, fit to upper portion of Trial i62 permeation curve

The Implicit solution fit in Figure 149 appears to be the best fit to the underlying permeation rate curve for the Trial i62 data.

SECTION 10.8 CONCENTRATION DEPENDENT DIFFUSION AND INTERMITTENT EXPOSURE

Solutions involving a constant diffusion coefficient did not fit the experimental data well, particularly in the early stages of permeation. The literature review revealed that concentration dependent diffusion of solvents through polymers could be expected and the Implicit solution was modified to permit this to occur. Crank (1975) proposed a number of different descriptions of concentration dependent diffusion, but the form taken by Uchytil et al. (1996) was used for this work.

Uchytil et al. (1996) used Crank's definition of a mean diffusion coefficient \( \bar{D} \) and exponential dependence of permeant concentration of the diffusion coefficient giving

\[
\bar{D} = \frac{1}{C_f - C_i} \int_{C_i}^{C_f} D(c) dC
\]

...............Equation 28 Mean diffusion coefficient

where

- \( C_f \) is the equilibrium solvent concentration on the membrane surface
- \( C_i \) is the initial solvent concentration on the membrane surface
- \( D(c) \) is the concentration dependent diffusion coefficient
Uchytil et al. (1996) set \(C_i = 0\) and \(D = D^* \exp(\gamma C_f)\) where \(\gamma\) was a "plasticisation coefficient" and \(D^*\) was the diffusion coefficient for low solvent concentrations. This gave, on integration

\[
D = \frac{D^*}{\gamma C_f} (e^{\gamma C_f} - 1)
\]

...Equation 29 Concentration dependent diffusion

Uchytil et al. (1996) found that the value of the argument, \(\gamma C_f\), in the exponential in Equation 29 was less than four, when fitted to acetic acid – polyvinyl alcohol systems, giving guidance to the expected value of \(\gamma\).

This form of concentration dependent permeation was added to the Implicit solution and adjusted to fit the experimental data by varying \(D\), \(S\) and \(\gamma\). The strategy used was to get a rough fit, then adjust \(D^*\) to ensure the peaks in the solution were in phase with the peaks in the experimental data. An effective wet time of 1.8 minutes was used in the calculations to account for the time for the solvent to evaporate.

![Figure 150 Concentration dependent diffusion](image)

The diffusion coefficient starts at \(1.6 \times 10^{-5}\) cm\(^2\) min\(^{-1}\) and increases by an order of magnitude, but oscillates in response to changing concentrations.
10.8.1 Fit of D(c) Implicit Solution to Published Intermittent Permeation Data

The fit of the concentration dependent diffusion "D(c) Implicit Solution" to the ASTM F1383-1996 data is shown in Figure 151, along with a fit of the plain Implicit solution.

![Figure 151 Fitting concentration dependent diffusion Implicit solution to ASTM F1383-1996 data](image)

At "A", the Implicit solution rises rapidly, but the concentration dependent Implicit solution is delayed. The non-zero initial permeation rate of the ASTM F1383-1996 data makes interpretation of this region difficult. At "B", the desired reduction in the permeation rate of the D(c) Implicit solution is very evident and the pattern at "C" is within experimental error. At "D", it can be seen that the phase of the peak in the Implicit solution is the same as that for the ASTM F1383-1996 data and the fit is almost exact. The Implicit solution has a much higher diffusion coefficient, and the phase of its peak leads the other data.

The greatly increased quality of the fit of the solution suggests that the exponential dependence of the diffusion coefficient described by Uchytil gives a better description of the permeation process than Fickian diffusion with a constant diffusion coefficient.

10.8.2 Fit of D(c) Implicit Solution to Experimental Intermittent Permeation Data

The same concentration dependent diffusion model data was fitted to Trial i60 data in Figure 152, but without further modifications to account for temperature changes.
Figure 152 Fitting Implicit solution with concentration dependent diffusion to Trial i60 data

At “A”, the diffusion coefficient appears too great, as the model data leads the experimental data. This may relate to the reduction in temperature of the sample from evaporative cooling. The process would have been quite complex at this stage as large temperature and concentration gradients would have been present. At “B”, the rising part of the curves, the fit is good and the "glitch" from evaporative cooling “C-D” indicated a rapid drop in the diffusion coefficient in the experiment.

The cumulative permeation estimate from the solution at 90 minutes was the same as that from trapezoidal integration of the ASTM data (34.6, 34.3±0.6 μg cm⁻²), so the exposure estimates were the same.

10.8.3 Application of D(c) Implicit Solution to Continuous Exposure Data

Whilst the fit to the intermittent permeation data appeared satisfactory, the solution should have been able to predict the permeation rate under conditions of continuous exposure. Good continuous exposure data had been obtained from the validation experiments for the Griffith cells, so this data were used for the comparison.
Figure 153 Fit of concentration dependent Implicit solutions to experimental data for continuous exposure

The fit of the solutions was poor, as the rapid permeation found in the experimental data was not matched by the model. A good fit could not be obtained by adjusting S, D and γ. Reducing the diffusion coefficient from 1.6E-5 to 1E-5 cm²min⁻¹ gave a similar steady state permeation rate and breakthrough time, but failed to match the shape of the curve. This lack of ability to predict continuous exposure reduced the confidence in the ability of the concentration dependent solution to be generally applicable to predicting the permeation of acetone through reference neoprene.

10.8.4 Summary of Features of the Intermittent Exposure Model

The following points summarise the implementation of the Crank-Nicolson Implicit model to calculate permeation of chemicals through CPC under conditions of intermittent exposure.

- The model has been shown to be validated against analytic models and published analytic data for continuous exposure, to give at least one point at which the model is known to work.
- The variables in the model are CPC thickness, initial concentration of chemical on each side of the CPC and inside the CPC material, the diffusion coefficient and solubility of the chemical in the CPC, and the wet-dry cycle lengths.
- Standardised conditions, based on figures given by Schwope et al. (1988) were used, as appropriate.
• If the diffusion coefficient is kept constant and the surface concentration of chemical is alternately maximum and zero, corresponding to wet and dry periods and the “inside” of the CPC is kept at zero concentration, then ideal, oscillatory permeation curves may be calculated for any given set of variables.

• The model can easily be extended to calculate random intermittent exposure and concentration dependent diffusion, though this implementation.

• It has been used to make predictions about the effect of cycle time on peak permeation rate and cumulative exposure.

• A gradient of wetting and drying could easily be built into the model.

The model has many limitation, including:

• It does not take into account rates of evaporation, any factors involving temperature

• The implementation of the model only used the concentration of the chemical on the inside of the glove to calculation of a concentration dependent diffusion coefficient. A more elaborate model would calculate a value of the concentration dependent diffusion coefficient for each layer.

• Lack of validation data for the model. An analytic model using Fourier analysis could be constructed to give a solution for a fixed diffusion coefficient and regular cyclic intermittent exposure. If this gave the same answers as the numeric model, then greater confidence in the data would result.

• The model cannot explain the processes that occur. If the model data fits the experimental data, this could be due to other factors.

SECTION 10.9 CONCLUSIONS

10.9.1 Numeric Solutions for Intermittent Exposure

• Spreadsheets can be used for both analytic and numeric solutions of models of permeation through CPC.

• The Explicit numeric solution gave an adequate representation of intermittent exposure, but appeared limited while a steady oscillatory pattern was being established (Appendix G). A more realistic solution was obtained with the Crank Nicolson Implicit solution.
10.9.2 Effect of Cycle Time

- Increasing the cycle time increased the prominence of the oscillatory part of the permeation curve but decreased the average permeation rate. The peaks became increasingly asymmetric with increasing cycle time.

10.9.3 Peak Permeation Rate and Cumulative Exposure

- Peak permeation rates dropped linearly with increasing cycle time until the peaks were effectively independent. At this stage, the peak permeation rate did not change.
- In contrast, the cumulative permeation was a simple linear function of the reciprocal of the cycle time, unless the cycle time was more than a third of the task time.

10.9.4 Random Exposure

- Random exposures can at least double the peak permeation rates, compared to regular cyclic exposures with standard conditions. Cumulative exposure was less affected as fluctuations averaged, although an average of 8% increase occurred with standard conditions.

10.9.5 Application of Implicit Solution to Experimental Data

- The Implicit numeric solution with a constant diffusion coefficient fell short of completely describing the permeation of acetone through reference neoprene under conditions of continuous and intermittent exposure, particularly in the early part of the permeation process.

10.9.6 Concentration Dependent Diffusion

- Concentration dependent diffusion produced an acceptable model for experimental acetone-neoprene data for intermittent exposure, with a good fit to published data and experimental data. The poorest fit was for the early permeation process.
- The concentration dependent diffusion Implicit solution still required further modifications to account for the effect of evaporative cooling on rapid reduction of the permeation rate.
- The concentration dependent diffusion Implicit solution failed to adequately describe permeation of reference neoprene by acetone under continuous exposure. The reasons for the lack of fit are not understood.

10.9.7 Permeation Indices Specific to Intermittent Exposure

- The index of Peak Permeation Rate may be of use in transient high concentrations of chemicals inside CPC where the toxic effect has a threshold, such as for skin
irritation. For random intermittent exposures, the Peak Permeation Rate could be increased by a factor of two or more.

- The index of Cumulative Permeation appears to be the most practicable permeation index where the chemical is more slowly metabolised or excreted, as it averages fluctuations due to intermittent exposure with both regular cyclic and random patterns.
CHAPTER 11. THESIS CONCLUSIONS

SECTION 11.1 AIM

This chapter summarises the findings on the design of permeation cells for testing chemical protective clothing under conditions of continuous and intermittent exposure and determines whether the objectives of this work were achieved. Recommendations for further work are given.

SECTION 11.2 ACHIEVEMENT OF OBJECTIVES

The findings of the Literature Review revealed areas of work needed. These were addressed through the objectives, during the course of this work.

A significant limitation in the applicability of this work is that almost all of the work on the two-chambered permeation cell was performed with acetone and reference neoprene. While this has produced data that should be replicable by other researchers, acetone is a small, polar, volatile liquid. It also evaporates easily.

11.2.1 Objective 1

To develop a permeation cell for continuous exposure, that approached the ideal design and produced data equivalent to the existing ASTM F739 standard cell.

Comprehensive design criteria to produce an ideal two-chambered permeation cell were developed, but the difficulty for one cell to satisfy all the criteria was recognised. The Griffith Mk2 cell was developed that satisfied most of the design criteria developed for permeation cells, including low cost, ruggedness and ease of fabrication. It had a particularly good collecting flow regime and produced almost zero backpressure on the test sample over a very wide range of collecting flows. Constraints of cost and simplicity prevented it from being suitable for use with corrosive chemicals and solid collection media, and limited its use with solid challenge chemicals. Replacement of the simple cell body with stainless steel or glass would allow corrosive material to be tested.

The Griffith cells had advantages over the standard ASTM F739 cell particularly with regard to collecting flow pattern. The collecting flow pattern in the Griffith cell was acceptable but that in the Griffith Mk2 cell was excellent with radial symmetry and no possibility of stagnation. Significant stagnation was mapped in the ASTM cell away
from the sample. The depth of the ASTM cell precluded visualisation of the flow pattern near the sample. Additional trials are needed to demonstrate the design advantages of the Griffith cells, particularly the Griffith Mk2 cell.

The Griffith cell and the Griffith Mk2 cell were demonstrated to be valid alternatives to the ASTM cell, in accord with the ASTM F739-1996 validation criteria. Here, the cell was within the limits for reproducibility and replicability using acetone and reference neoprene using the ASTM F739-1996 test protocols. The Griffith cell and Griffith Mk2 cell were also equivalent to each other, using the much more precise permeation data generated in this research.

The difficulty in producing reliable normalised breakthrough time data at a low permeation rate impeded the automation of permeation testing. This difficulty could be overcome by the use of Lag Time.

11.2.2 Objective 2

To characterise operational parameters that would affect the measurement and interpretation of permeation data for conditions of continuous exposure.

The permeation rate in the Griffith cells was unaffected by the flow rate (at least for acetone as a challenge chemical) through the collecting volume over a wide range of flows. A drop in permeation rate was found in the Griffith small cell at very low flow rates, but direct measurements at this low flow rate range could not be made in the other cells due to the measurement range of the PID.

The pressure build-up with collecting flows was greater in the ASTM cell than the Griffith Mk2 cell, but most of the pressure build-up was due to the test rig downstream of the cells. However, the pressure build-up with flow rates normalised to the exposed sample area in the Griffith Mk2 cell was far less than that in the ASTM cell. The distension of the reference neoprene from pressure build-up in the ASTM and Griffith Mk2 cells was negligible under normal operating conditions.

Solvent depth over the test sample did not affect permeation with acetone, as long as the sample remained wet. It is expected that this finding could be extended to other single chemicals.
Thickness estimates of CPC using a dial gauge are likely to underestimate the thickness of the test sample due to the pressure of the dial gauge foot. For reference neoprene, this underestimation was 2.3 μm. This resulted in an underestimate of SSPR of 0.5%, and overestimate of BT and LT of 1%, within normal experimental error. In addition to the pressure effect, it was also found that the release of a dial gauge stem close to the sample produced an embedding of the foot in the sample of up to 1.5 μm in reference neoprene, which produced a corresponding underestimate of the sample thickness. Sample weight correlates poorly with sample thickness. The density of the neoprene may vary, with thinner samples of the neoprene being denser. This limits the use of mass as a measure of thickness. A vacuum plate has the potential to improve the measurement of thickness of samples, particularly if they do not lie flat. However, a 10% loss of vacuum (10 kPa) resulted in a 1 μm decrease in the estimation of the sample thickness, through deflection of sintered glass plate.

Low level emissions of a volatile substance emanated from the reference neoprene sample on addition of acetone or on tightening of the cell clamp. While these emissions were below the nBT permeation rate of 0.1 μg cm⁻² min⁻¹ they would compromise more sensitive measurements. Gentle heating in a vacuum oven removed most of this contamination suggesting a need for standardised sample pre-treatment prior to permeation testing. The ASTM F739-1996 method for estimating detection limits permits an optimistic estimate of the minimum detectable permeation rate by the use of an aluminium sample in place of a CPC sample as it was found that the sample itself may produce low level emissions. It was though that this emission was water, as high levels of humidity water is reputed to decrease, not increase the response of PID detectors. Water itself has an ionisation potential (12.59 eV) well above that of the PID lamp (10.8 eV), but it may be still prudent to directly check the effect of trace amounts of moisture on the PID response.

The experimental problems in establishing an index relating to breakthrough with multiple cell systems were entirely overcome with the use of Lag Times. The measurement of nBT required a very low background, something that was unable to achieved with carryover from one cell to another whilst using a single detector. LT estimates are very a much more precise than BT estimates and were demonstrated to be
less affected by detection limits, as it is derived from the extrapolation of permeation data greatly in excess of the nBT permeation rate of 0.1 \( \mu \text{g cm}^{-2}\text{min}^{-1} \).

Trials with toluene vs PVC gloves as a worst case scenario with great variability in the data. Trials with acetone vs reference neoprene were considered to be a realistic best case scenario as the material came from a sheet rather than a CPC garments and was selected by ASTM Committee F23 for its uniformity. For the latter that SSPR could adequately discriminate between samples with the three measurement recommended by ASTM F739-1996. At best, BT could discriminate a 30% difference in BT values. LT performance was better than SSPR in the best case scenario but not as good as SSPR in the worst case scenario where 36 measurements were required to discriminate a 30% difference in the BT values. Because LT is suited to testing with multiple cell systems, it is a more reliable indicator of CPC performance than BT, but as little LT data has been published, it would serve to supplement rather than replace BT in ranking CPC choices at this point in time. This is an important factor when good science requires multiple measurements and automated multi-cell test systems with a single detector provide a more economical approach than a single cell system.

Both LT and BT are indicators of a rapid increase in permeation rate but they have very different derivations. When the analytic detection limit is poor, the BT is numerically the same as the measured LT.

Modelling

In modelling permeation, it was found that Breakthrough Times were extremely sensitive to analytic detection limits, whereas Lag Times were remarkably unaffected even when the analytic detection limit is half of the Steady State Permeation Rate. Thus, it is theoretically valid to use the integral of open loop Permeation Rate data to generate Cumulative Permeation curves to calculate Lag Times.

Analytic solutions of permeation with a constant diffusion coefficient and constant solubility, fell short of completely describing the permeation of acetone through reference neoprene under conditions of continuous exposure. Caution is warranted in applying solutions based on estimates of the diffusion coefficient from Lag Times to estimate toxic exposures in the transition phase before steady state permeation occurs.
11.2.3 Objective 3

To investigate an approach to permeation testing for low vapour pressure, water insoluble chemicals and solids, that circumvents the requirement for the chemical to evaporate or dissolve in a collecting medium.

A novel gas pressurised ATR permeation cell was demonstrated to produce permeation data with liquids, mixtures and solids, showing the great versatility of the approach in measuring the breakthrough of otherwise difficult to measure chemicals under conditions of continuous exposure. The utility of the cell was demonstrated with liquid mixtures and a volatile solid (naphthalene), at temperatures in the range 20 – 45°C. The method is simple and fast, and promises a reasonable level of reproducibility. While not performed, measurements of gases and vapours would also be possible. The Griffith ATR cell requires further testing with a range of solids (including granules) with different vapour pressures, water insoluble chemicals, and mixtures of chemicals, particularly agricultural chemicals, to test its full potential.

Pressurising the cell with a gas held the test sample against the ATR crystal in the limited trials performed, however more trials would have to be performed to determine whether this ability extended to a wide range of chemicals and CPC polymers. The low gas pressure in the cell may still compress very compliant samples.

BT's and LT's may be estimated by ATR and this may assist in the ranking of CPC choices. Relative SSPR estimates should be possible, but nBT estimates require the quantification of the nBT permeation rate of 0.1 μg cm⁻² min⁻¹. This is not yet possible. Further development of the ATR theory for CPC permeation may permit better estimates of calibration factors and permit permeation measurements in μg cm⁻² min⁻¹.

ATR measurements of permeation may be approximated to closed loop permeation with a small collecting volume that is the last 2 μm of the test sample, plus any residual volume between the surface of the sample and the ATR crystal. The collecting volume will eventually saturate with permeant and this may preclude derivation of an open loop SSPR value, as build-up of permeant in the collecting volume can reduce the permeation rate before conditions similar to steady state permeation with an open loop cell are reached. This limitation may not be significant in practice with molecules of low volatility, as a major application of permeation data is to rank choices of CPC.
BT and initial permeation rate could be used to assist this ranking. The theory of ATR applied to CPC permeation does not yet permit the estimation of a SSPR value.

11.2.4 Objective 4

*To advance the approaches to permeation testing under conditions of intermittent exposure and develop a model to simulate permeation patterns.*

Intermittent exposure cell development

An automated intermittent exposure cell, constructed to predetermined design criteria, was tested against the acetone-reference neoprene permeation data from the ASTM F1383-1996 intermittent exposure cell. It gave a near identical permeation curve only when the reference neoprene was pre-equilibrated with acetone vapour, suggesting that the ASTM F1383-1996 data were similarly pre-exposed. With samples unexposed to acetone vapour, a different permeation curve resulted, with a zero initial permeation rate, and a permeation curve that more slowly developed the characteristic oscillatory shape of cyclic intermittent exposure.

Reproducibility for cumulative permeation estimates using the Griffith Mk2 Intermittent exposure cell appears similar (9.9% vs 7.7%) to the ASTM F1383 intermittent but the data, but the number of data is too small for definite conclusions. This was due to the length of time to develop the control software and then the cost of nitrogen.

Intermittent permeation cell data published in ASTM F1383-1996 had a reported wet time of one minute in a 15-minute cycle. However, the effective wet time derived from comparing contact time and resultant cumulative permeation rates for continuous and intermittent exposures, suggested a 1.8 minute wet time. If intermittent exposures are to be compared, then the actual time that solvent remains in contact with the sample is important.

The Griffith Mk2A Intermittent exposure cell with its large solvent reservoir performed like the Griffith Mk2 Intermittent exposure cell, but greatly extended the time between refilling of the reservoir, permitting extended trials.
Experiments with the Griffith Mk2 Intermittent exposure cell

Dye studies on the drying flow patterns in the Griffith Mk2 Intermittent exposure cell revealed the offset inlet port for the drying gas produced a swirling flow that appeared to be close to optimum. It produced a vigorous flow next to the test sample provided rapid clearance of the wet side of the cell and was thought to efficiently remove residual solvent.

A significant "glitch" that occurred in the data was shown to be due to warming of the sample by the solvent in the wet time and evaporative cooling of the sample at the start of the dry time. The lack of a glitch in the ASTM F1383-1996 data might relate to the different drying flow rate and flow pattern in the ASTM F1383-1996 cell, the frequency of measurements and the manual operation of the cell. The choice of a 15-minute cycle may have also obscured the glitch in the ASTM F1383-1996 data, as it would have occurred at a time that the permeation rate was already falling.

Acetone-reference neoprene permeation rate fluctuations (the "glitch") were explained by cooling of the sample by the evaporating challenge solvent and the subsequent temperature effect on permeation. Over a wide range of drying flow rates, the drying flow rate with a dried sample did not in itself have a significant effect on permeation except a possible stretching of the sample due to pressure when the drying flow rate was 4000 mL min$^{-1}$.

When permeation rate was measured during the wet time, a simple inverse relationship was found to exist between the permeation rate and cycle time for short cycle times. During the wet time, the temperature of both the wet and dry side of the sample was the same. With evaporative cooling during the drying time, a temperature gradient of 10°C or more developed. For long cycle times, 15 minutes or longer, the underlying permeation rate became important and the effects of evaporative cooling less important.

When the temperature in an experiment is required to be reported, such as in ASTM F739-1996 and ASTM F1383-1996, the location of the measurement and the type of temperature sensor will affect the reported temperature. Immersing the permeation cell in a water bath or a gas chromatography oven would regulate the cell temperature but have little effect on the temperature of the sample during intermittent exposure. As the
drying flow rate was not specified in ASTM F1383-1996, it would be difficult to replicate permeation rates in different laboratories.

There is a need for additional trials on the Griffith Mk2 Intermittent cell with other solvents, particularly less volatile solvents, more viscous solvents are mixtures of solvents. Less volatile solvents would test the efficiency of the drying flow pattern and permit comparative studies on the relative cooling of different drying flow rates and flow patterns. Viscous solvents may not wet the sample as well, drain slower and perhaps affect the movement of the return valve. Mixtures of solvents could introduce additional complications including the effects of differential evaporation.

Trials monitoring the solvent concentration in the drying air stream may indicate more about the effective wet and dry periods under intermittent exposure. This work only monitored the permeation rate and the surface temperatures of the sample.

Modelling intermittent exposure

Analytic and numerical solutions to a Fickian diffusion model of permeation through CPC were implemented using a spreadsheet. Explicit numerical solutions gave an adequate representation of cyclic intermittent exposure, but overestimated permeation rates while a regular oscillatory pattern was being established. A more realistic model was obtained with the Crank Nicolson Implicit solution.

Peak permeation rates with a regular, short wet time, dropped linearly with increasing cycle time until the peaks were effectively independent. At this stage, the peak permeation rate did not change. In contrast, the cumulative permeation was a simple linear function of the reciprocal of the cycle time, unless the cycle time was more than a third of the task time. Increasing the cycle time increased the prominence of the oscillatory part of the permeation curve but decreased the average permeation rate. The peaks became increasingly asymmetric with increasing cycle time.

Random exposures can at least double the peak permeation rates, compared to regular cyclic exposures with standard conditions. Cumulative exposure was less affected than peak permeation rates, as the random fluctuations averaged. However, although an average of 8% increase occurred with standard conditions due to the asymmetric shape
of the peaks in the permeation curve. More of the permeation had occurred before the middle of an average cycle.

The index of Peak Permeation Rate may be of use in transient high concentrations of chemicals inside CPC where the toxic effect has a threshold, such as for skin irritation. For random intermittent exposures, the Peak Permeation Rate could be increased by a factor of two or more. The index of Cumulative Permeation appears to be the most practicable permeation index where the chemical is more slowly metabolised or excreted, as it averages fluctuations due to intermittent exposure with both regular cyclic and random patterns.

The Implicit numerical solution with a constant diffusion coefficient fell short of completely describing the permeation of acetone through reference neoprene under conditions of continuous and intermittent exposure, particularly in the early part of the permeation process.

Concentration dependent diffusion produced an acceptable model for experimental acetone-neoprene data for intermittent exposure, with a good fit to published data and experimental data. The poorest fit was for the early permeation process. The Implicit solution with exponentially concentration dependent diffusion failed to adequately describe permeation of reference neoprene by acetone under continuous exposure.

**SECTION 11.3 FUTURE DIRECTIONS**

**Griffith Mk2 cell**

Further research using the Griffith Mk2 cell and the ASTM F739 cell to measure permeation of a range of chemicals and CPC materials is planned, in order to further demonstrate the superior performance of the Griffith Mk2 cell and produce permeation data for use in the workplace. Efficient cell designs are needed to overcome the problems in measuring the true steady state permeation rate recently shown by Anna et al. (1998).

**Development of Standards**

There is a need for further work to demonstrate reproducibility and replicability of the intermittent permeation data. There is a need to adopt standardised experimental conditions for trials of permeation data from intermittent exposure cells for both
repeatability within laboratories and reproducibility between laboratories. These should include the test chemical, test material, exposure conditions, nominal test temperature, drying flow rate and measurements of the surface temperature of the exposed and unexposed sides of the sample during the cycles. The latter may point to differences between cells and test set-ups.

Permeation Indices
The number of tests to adequately determine the uncertainties in the measurement of indices has not received sufficient attention, nor is there awareness of the unpublished uncertainties in data used to rank CPC selections. These issues need to be further explored. There is also need for more debate on the most appropriate indices to represent the non-continuous nature of workplace exposures to chemicals. This work has indicated that the assumption of a constant diffusion coefficient in modelling permeation may be adequate, though the experiments were restricted to acetone and neoprene. A greater sophistication of approaches to the theory of permeation through CPC polymers appears to be warranted.

The theoretical work on permeation indices for intermittent exposure in this work is a start, but the ultimate aim should be permeation indices that relate to the toxic effect of the chemical on the user. It must involve the skin and the local and system toxic response of the body.

Flow patterns in cells
There is scope for additional quantitative studies of cell clearance to measure the concentration of a dye or tracer gas in the effluent flow and to develop other methods for revealing regions of poor flow next to the test sample. One such method may be to monitor to concentration of permeant in the drying flow. Good flows should more rapidly reduce the challenge chemical concentration to a predetermined low level.

Effect of collecting flow rate on permeation
More elaborate experiments with detectors with a greater range of detection or diluted flows to the PID are required to detail the lower flow limit for use with the Griffith cells.

Griffith ATR permeation cell
The potential of the pressurised Griffith ATR permeation cell to investigate the permeation of difficult-to-measure chemicals and complex mixtures has not yet been fully explored, particularly with laminated glove materials. Laminated gloves cannot be dissolved in solvents and evaporated onto an ATR crystal as it destroys its structure. The pressurisation of the Griffith ATR permeation cell permits direct measurements on excised samples.

There is a need to further develop the ATR theory for CPC permeation to better estimate calibration factors for converting absorbance into permeation rates, and to establish permeation rates to determine normalised breakthrough times. At the moment, only crude ranking of CPC choices is possible, with BT and initial permeation rates as a guide to the ranking. Estimates of nBT and SSPR are not yet possible.

There is also an untapped potential in the method to characterise permeant-polymer interactions during the permeation process by interpreting changes in the polymer spectrum derived from the Griffith ATR permeation cell. Bommannan *et al.* (1990) noted a "blue shift" in skin lipids from changes in structure of the lipids. If solvents affect the structure of polymers, it may be possible to investigate these changes during the permeation process using ATR. This would be a direct measure of solvent polymer interactions. This knowledge may give insights into the interaction and changes in interaction of challenge chemical and CPC polymer during the permeation tests.

**Intermittent exposure cells**

There is scope for refinement of the test methodology using the Griffith Mk2 Intermittent exposure cell with a range of chemicals including less volatile and more viscous solvents, and a range of CPC samples. Installation of the extra valves and control cards to permit the simultaneous use of eight cells with the *GloveTest* system is being considered.

There is a need for direct comparison of the Griffith Mk2 Intermittent exposure cell with an ASTM F1383-1996 Intermittent exposure cell. There is a particular need to measure the drying flow rates and the surface temperatures of the samples in both cells.
When data are available for a range of chemicals and CPC types, the models developed to emulate the permeation of acetone through reference neoprene may be applied. Extensions of the intermittent solution to Crank-Nicolson model to account for temperature gradients caused by evaporative cooling would increase understanding of the permeation process under conditions of intermittent exposure.

SECTION 11.4 CONCLUSION

This work has been characterised by fundamental questioning of the existing technology and methodologies associated with permeation testing through chemical protective clothing. This has resulted in the development of new permeation cells based on explicit design criteria. It includes a series of investigations of the factors associated with permeation measurement and their interpretation, including temperature, drying and collecting flow rates, flow patterns, depth of solvent, pressure on the sample and approaches to sample thickness measurement. Permeation indices were explored, to determine the most appropriate indices to rank selections of CPC. LT was more suited to automated multi-cell permeation test systems with a shared detector than BT or nBT, but LT measurements are rarely published, limiting the use of the index. SSPR was found to be a more sensitive index than BT in ranking CPC choices.

The research culminated in the development of an automated intermittent exposure cell and modelling of intermittent exposure, with an exponentially concentration dependent diffusion coefficient providing an acceptable fit when compared with published data. The ATR cell demonstrated the potential for testing previously difficult-to-measure chemicals, though more work is required to demonstrate the utility of the cell with other difficult-to-measure chemicals. BT and LT can be measured, as can relative permeation rates, though nBT estimates cannot yet be made due to the difficulty in providing a calibration factor. The development of the theory of ATR applied to CPC to permit the estimation of calibration factors is needed.
APPENDIX A. OTHER CELL DESIGNS

SECTION A.1 SCOPE
This appendix briefly reviews some of the cell designs for testing the permeation of chemicals through CPC, that have been published in the peer reviewed literature including PhD theses. The only broad review of cell designs that could be found was by Henry (1990), though Mellstrom et al. (1989) compared three cells. The work by Graham in 1829 is included for completeness, through his work was performed for testing membranes, not CPC.

SECTION A.2 HISTORICAL
Some of the historical developments in measuring permeation are worth noting as the quality of the work was high and some of the approaches have been forgotten and then re-invented.

A.2.1 Graham 1829
The first understanding of the concept of diffusion as a molecular process was by Graham, including Figure 155.

Figure 155 18th Century Sewer Worker, from Smart and Griffiths (1982)
Rubberised fabrics were waterproof and early concerns appeared to be with penetration - that would result in getting wet, not permeation.

SECTION A.3 PERMEATION CELLS FOR CPC
The cells are presented in chronological order with brief notes, but this is not an exhaustive catalogue of cell designs. As most of the cells have not been used by the
author, the utility of the cells have been surmised from published photographs, descriptions and published results of permeation experiments using the cells. As a whole, they give a range of properties that an ideal cell may exhibit.

**A.3.1 Linch’s permeation cell, 1971**

Henry (1990) pictured an early permeation cell by Linch (1971). The design requires an excised sample and the cell appears to be capped with a rubber stopper. The six wingnuts would clamp the horizontal test sample. A port to either collect or introduce a collecting medium is evident in the lower half of the cell.

![Figure 156 Linch's cell 1971, from Henry 1990](image)

The cell would have kept the sample wet due to the horizontal orientation, but it would be slow to use with so many wingnuts and would probably have a large dead volume. It could not be used with intact garments.

**A.3.2 Weeks' cell, 1977**

Weeks and Dean (1977) published the design of a cell that is remarkably similar to the ASTM cell. The cell is simple, but fragile and requires the sample to be held in a vertical orientation. The clamping appears inadequate and it has most of the disadvantages of the ASTM cell.
Sansone and Tewari (1978) described the AMK cell in trials with 24 solvents and 6 glove materials. It was made of glass and was chosen for its low challenge chemical volume (~2 mL). The halves were held together by a sprung clamp and "O"- rings sealed the cell. The cell was used horizontally at room temperature using water as the collecting medium. Samples were taken at 0.5, 1, 2, 4, 6, 8 hours with a 2 μL micro-syringe for analysis by GC- FID. The cell was patented by the Radian Corporation. It was designed only for use with liquids and could not be used in an open loop mode.

A similar cell was depicted by Henry (1990), but with side ports for filling with test chemical and removal of permeant is shown in Figure 158. A clamp, similar to that used by chemists for clamping glassware, holds the halves together.
A variant of the AMK cell for open loop permeation testing was compared with a bored out ASTM F739 cell by Berardinelli et al. (1983), with comparable, but statistically different results. The collection volume of this cell was 20.4 mL.

The AMK cell does not appear to be in common use.

**A.3.4 Williams' cell, 1979**

The cells designed by Williams (1979, 1980) appear to be rugged, with similarities to both the ASTM F739 and ISO cells.
The internal working of the cell are shown in Figure 162.

The entry flow is off centre like the ISO cell and there would be "dead" areas in the flow pattern. It is held together with a 3-bolt flange like the ASTM cell, but the sample is horizontal like the ISO cell. The Figure 161 does not show the cap or springs. A variant of the cell was published by Williams in 1980, using a central clamp with a whole garment (Figure 163).
The flange clamps have been changed to a single, central clamp and a torque screwdriver was used on the clamp, though the pitch of the thread was not given. This detail limits estimations of clamping forces.

The cell is similar to the ISO cell and would have a better collecting flow pattern than the Williams 1979 cell due to the central inlet. The inlet and outlets through the side would make the cell easier to handle than the ISO cell. Williams compensated for backpressure from the gravimetric charcoal tubes used to collect permeant by altering the depth of test chemical. A torque screwdriver was used to tighten the bolts. This cell is closest in design to the Griffith cell.

A.3.5 **Sansone’s cell, 1980**

Sansone and Tewari (1980) used a stainless steel permeation cell shown in Figure 165, with a wire mesh disk to support the test sample and prevent it from sagging. Benzene
vapour was introduced to one side of the sample at 10 mL min\(^{-1}\) and air at the same rate collected any permeant.

![Figure 165 Sansone's cell, 1980](image)

The wire screen would tend to trap a thicker boundary layer of permeant, which would not be disrupted by the low collection flow rate. The cell could be expected to have a poor flow pattern and has a larger than needed collecting volume.

**A.3.6 ASTM F739 cell, 1981**

The ASTM cell was adopted by the American Society for Testing and Materials from the design published by Henry and Schlatter (1981) in the American Industrial Hygiene Association Journal. Its acceptance as the standard cell may have limited the development of better designs, but it has ensured some uniformity of testing.

![Figure 166 ASTM F739 cell, 1981](image)

This cell became the Standard cell - so there was no need for validation studies. It can test liquids and gases, but not solids and the sample has a large area for analytic sensitivity. An alternate smaller (25 mm) version is available. The sample may be observed during testing. However the cell is fragile, expensive, has a poor flow pattern.
on the collection side and a large collecting volume. It has multiple bolts to clamp the cell, making assembly slow and potentially uneven. The use with a vertical test sample creates pressure gradient on the sample, except when liquid or gases are used on both sides of the sample. The taps on ports limits flow through cell (Perkins and Ridge, 1986a). The large sample limits "random" selection to palm, back and cuff.

![Figure 167 Commercial ASTM F739 cell](image)

The cell is commercially available, giving it wide acceptance as the standard cell.

**A.3.7 Nelson's cell, 1981**

![Figure 168 Nelson's cell, 1981](image)
The cell designed by Nelson et al. (1981) was used with organic solvents and designed to permit a 25 Lpm flow through a Miran 1A infrared analyser. The large dead volume of the cell and overflow trap (Figure 169) would be much smaller than the 4 L dead volume of the Miran.

![Diagram of Nelson's system, showing flow trap and Miran 1A analyser, 1981](image.png)

**Figure 169** Nelson’s system, showing flow trap and Miran 1A analyser, 1981

### A.3.8 ISO cell, 1986

This cell is described by Leinster et al. (1986) and by Mellstrom (1991b).

![Diagram of ISO cell, 1986](image.png)

**Figure 170** ISO cell, 1986

The cell is rugged, simple to fabricate and easy to decontaminate. It has some acceptance as a standard cell (ISO 6529 (New Working Draft), 1997). The flow pattern should be better than for the ASTM cell. The exit at the base prevents the cell from being free standing and multiple bolts prevent use with intact garments. There appears to be an unnecessary dead volume but the cell could be adapted to test gases and solids.

### A.3.9 Test cup

Henry (1990) pictured a "test cup" permeation cell similar to the ISO cell for permeation testing. The origin of the cell was not clear. Unlike the ISO cell, it appears to be free standing.
A.3.10 Stampfer's cell, 1984

A cell to test polychlorinated biphenols as described by Stampfer et al. (1984a) is shown in Figure 172. It appears to be made from hydraulic fittings and would require a relatively large volume of challenge chemical and have a large collecting volume.

The cell appears unnecessarily complex, and would only be suitable for closed loop testing.

A.3.11 Davis' cell, 1986

Davis et al. (1986) found that "frequent breakage" of a ASTM F739-81 cell was unacceptable and constructed a stainless steel version with the same internal dimensions. Davis claimed that "experiments employing the same challenge and glove material revealed no difference in results between the two cells." The test data and the statistical tests permitting this claim were not given.
The cell would be rugged but expensive to make, and the metal construction would limit the range of test chemicals and not allow observation of the test sample. Except for ruggedness, it appears to offer few advantages over the ASTM cell.

**A.3.12 Forsberg's cell, 1986**

Forsberg and Faniadis (1986) described a simple test cell that had central clamping like the Griffith cells.

The cell is simple and can be used with intact CPC garments. It would be quick to assemble due to the single clamp, but it may be difficult to align the two sections, as no keying of the sections is apparent. There is a large (25 mL) collecting volume and the collecting flow patterns are not directed at the test sample. The cell is only suitable for...
liquids and there is no way to "top up" the cell during use, as the cell would be inverted with test chemical during assembly.

**A.3.13  ASTM F 903 penetration cell, 1987**

A special cell for chemical penetration was recommended by ASTM (ASTM F903, 1987).

![Figure 175 ASTM Penetration Rig, 1987](image.png)

Figure 175 ASTM Penetration Rig, 1987

Only permeation, not penetration, was considered in this work. This, and other penetration cells, will not be further discussed.

**A.3.14  Cvejanovich's cell, 1989**

Cvejanovich's PhD thesis (1989) shows a simple 102 mm diameter cell, made of stainless steel, that held a 50 mm test sample between the halves with bolts. It was used with the sample in the vertical position, like an ASTM cell.

![Figure 176 Cvejanovich's stainless steel cell, 1989](image.png)

Figure 176 Cvejanovich's stainless steel cell, 1989

The cell appears more rugged than the ASTM cell, and the collecting volume appears much smaller. However the cell has unnecessary bulk and cannot be used with intact
CPC garments. Poor flow patterns could be expected and it may be difficult to tighten bolts evenly without a torque wrench.

**A.3.15 Mellstrom’s cells, 1989**

Three cells were compared by (Mellstrom *et al.*, 1989) Mellstrom *et al.* (1989). The stainless steel "FMD" cell had opposing inlets and outlets for the collecting flow and a cover glass sealing the cell, but permitting observation of the sample. It has the smallest volume of the three cells. The collecting flow near the test sample would have been poor.

![Figure 177 Mellstrom's FMD cell, 1989](image)

A second cell, the "R" cell, was also made of stainless steel and appears to be a larger version of the "FMD" cell.

![Figure 178 "R" cell, with modification, 1989](image)

Experiments were performed on the "R" cell, directing the collecting flow with a Teflon tube (dashed lines)

A third cell, the "T" or "Scandcell", was made of Teflon and had the collecting flows adjacent. It used a single central clamp, permitting its use with whole garments.
In triplicate trials of the cells, with 5 mm of solvent, it was found that the collecting flow rate and cell design affected the permeation rate, but not the breakthrough time. The relationship between permeation rate and collecting flow rate was re-examined in the literature review (Chapter 2). Redirection of the flow in the "R" cell with the tubing decreased the measured permeation rate. Mellstrom attributed this to poor mixing and possible laminar flows in the collecting volume.

Although a number of desirable features were noted by Mellstrom in the three cells, a new cell design that incorporated all these features was not given.

**A.3.16 Ehntholt's cell, 1990**

Ehntholt et al. (1990) performed permeation measurements on chemicals with low vapour pressures and poor water solubility, both of which preclude the use of a gas or water as a good collecting medium. Other chemicals work, but may interact with the sample. Ehntholt's cell claims to be a "slightly modified" version of the ASTM F739-85 cell. In reality, the two sides of the cell had completely changed and the cell orientation was horizontal. Only the exposed sample area remained the same.

The cell was developed to allow a solid - silicon rubber, to be used as the collecting medium, as "no accepted collecting method for monitoring the permeation of the active ingredients in such formulations exists..." Direct interfacing of a detector with the sample appears not to have been considered.
The cell has potential to test low vapour pressure and water insoluble chemicals, but it is cumbersome and fragile. The claim to be only "slightly modified" from an ASTM cell would be difficult to substantiate. The design that requires removal of the silicon rubber collecting medium for each measurement would limit the number of measurements. Problems maintaining contact between the silicon rubber collecting medium and test sample have been reported (Pinette et al., 1992f).

A.3.17 Degradation test cell

Henry (1990) also pictured a "degradation test cell", similar to Sansone's test cell. It appears that the cell would be used to observe physical changes in the test sample and would equate to immersion testing.
A.3.18         Joh’s skin permeation cell, c1990

A number of cells have been published for use with skin, requiring thermostating to emulate skin temperatures. One such cell is shown in Figure 182.

Figure 182 Joh’s skin cell, c1990

From Johnson and Anderson, 1990

Permeation of skin has attracted considerable interest due to the commercial applications of transdermal drug delivery.

A.3.19         Fricker’s cell, 1992

Fricker’s PhD thesis (1992) detailed a cell designed to measure the permeation of solid chemicals through CPC. The essential element in the design was direct access to the CPC sample, permitting the loading of the cell with a solid chemical after the cell was assembled. The cylindrical geometry is the simplest form that would permit this arrangement. The plunger ensured the solid chemical was kept in contact with the CPC.
There is some ambiguity about the size of the cell, as the proportions of the cell in Fricker's sketch do not match the published dimensions. The cell is the only published cell design specifically for testing solids, but it could be used with liquids. It may have poor flow patterns on collection. It has a large collecting volume and the plunger appears larger than needed. The exposed area is not precisely defined, as the sealing O-
ring is large. The cell has multiple bolts to clamp the cell, making assembly slow and potentially uneven. It cannot test intact garments due to the multiple bolts holding the cell together. The small bore of the ports would limit the flow rate, although this may not be a real limitation if used with low vapour pressure solids and instruments like gas chromatographs.

SECTION A.4 GRAVIMETRIC CELLS

A number of cells have been developed that rely on weight loss to determine Breakthrough Time and Permeation Rates. By their nature they are insensitive to components in a mixture and cannot easily be ventilated without upsetting the performance of the balance.

A.4.1 Schwope's permeation cup, 1988

A permeation cup for gravimetric measurement of permeation rates was described by Schwope et al. (1988b). The design criteria were noted in the literature review (Chapter 2).

![Figure 185 Schwope's permeation cup, 1988](image)

The cell allows sensitive analytic balances to determine permeation rates by weight loss, but the heavy construction would limit the use to less sensitive balances. It is possible that a layer of stagnant permeant could build on air side of the sample, reducing the concentration gradient through the test sample.

A.4.2 Stull's gravimetric cell, 1992

Stull et al. (1992c) designed a gravimetric cell for field use. The design is similar to that of Schwope et al. (1988b) except that the body of the cell appears to be pressed rather than machined. Comparable results were obtained in a round robin, and the method was considered useful as a field test.
Figure 186 Stull's permeation cup, 1992
APPENDIX B. GLOVETEST RIG, CELLS AND ACCESSORIES

This Appendix gives further details on the GloveTest hardware, including the evolution of the rig from a prototype to the present version, further details on the permeation cells, and accessories used with the rig.

The GloveTest rig operates on a relatively simple principle. Any solvent that permeates a membrane can be detected in a carrier gas that passes over the opposite surface. The concentration of the solvent in the carrier gas is proportional to that which has passed through the membrane. This is only true until the carrier gas approaches saturation. For the flow rates, cells and choice of solvents used in these experiments, this was always so. The rig consists of seven parts:

1. The carrier gas distributor.
2. Flow regulation of the carrier gas.
3. Sample holding cells.
4. Flow switching system.
5. Solvent detector and flow meter.
7. Software Control System (GloveTest).

SECTION B.1 PROTOTYPE GLOVETEST RIG

A permeation testing rig was built during a funded project (Bromwich et al., 1997) of which the author was the chief investigator. The project was concluded during this work. The design concept was retained, but the rig was rebuilt and the software considerably expanded and improved.

The design evolved to allow sequential measurement of up to eight cells, sequenced by a commercial Programmable Logic Controller (PLC) so that a single detector could be used. Other researchers have used multiple detectors (Berardinelli et al., 1990), avoiding this complexity, but adding considerably to costs and the need to calibrate multiple detectors. It was quickly realised that generic multi-channel Analogue to Digital (A-D) computer boards were available at much the same cost as a logging digital volt meter and that PLC cards were also available for personal computers. With a cheap personal computer at the heart of the system, interrogating a 12 bit 16 channel A-D board and controlling a 16-channel PLC card, a much more powerful and flexible test
rig was constructed for less. A new programming language, Visual Basic 3.0 Professional (Microsoft) was available, which was used to construct a powerful control, display and analysis system for testing CPC (see Appendix B). Additional measurements of temperature and flow were relatively easy to accomplish.

The prototype rig was mounted with screws and “Velcro” tape on a large board to keep it together and permit rapid modifications. The prototype layout is shown in Figure 187.

![Figure 187 Prototype GloveTest rig on mounting board](image)

The visible features in Figure 187 are described. The nitrogen distribution manifold "A" supplies the precision metering valves "B" for the permeation cells "C" and "D" which are held in the clamping frame. The collecting flow from the cells is diverted to the PID "G" or the waste line "J" by the poppet valves "E" that are actuated by the solenoid valves "F". The collecting flow to the PID "G" is periodically switched to the mass flow sensor "H" (and temperature sensor, not visible). The poppet valves "M" are used to wash and fill the Tedlar sampling bags used to generate atmospheres to calibrate the PID. The solenoid valves "L" are used to automatically cut the nitrogen flow at the end of an experiment.

### B.1.1 Carrier Gas and Flow Control

As constructed, the carrier gas was nitrogen rather than air, with flow controlled by metering valves attached to a manifold to ensure even pressure distribution. This ensured a high purity of carrier gas and removed potential carbon dioxide and water vapour infrared interferences from the flow. The supply pressure at the manifold (about 90 psi, 600 kPa) was much greater than the pressure at the cells (less than 10 Pa) making the flow through each metering valve independent of the flow through the other metering valves.
A manual control valve and solenoid were placed between the nitrogen supply and the inlet manifold. This solenoid cut off the flow of nitrogen after the rig had run for its predetermined time to eliminate nitrogen wastage. A problem experienced during the early testing of the rig was bottles of nitrogen gas running out during a trial. As actual nitrogen usage was more precisely known, this became less common.

**B.1.2 Photoionisation Detector**

The project relied very heavily on the HNU 101 photo-ionisation detector (PID) that could easily detect the solvents used in the project and had a remarkably fast response time, allowing rapid cycling between cells and flush cycles. The 10.2 eV lamp in the PID gave a good compromise between sensitivity (the ability to measure a solvent) and selectivity (the ability to distinguish between solvents). It is insensitive to most atmospheric gases including oxygen, nitrogen, carbon dioxide and water vapour.

![Figure 188 HNU 101 photoionisation detector](image)

The detector was modified by making the inlet shorter, rather than using the standard long inlet probe. This made the sampling head more compact and reduced the dead space in the measuring system, giving a marginally faster response of the detector to changes in concentration in the carrier gas from the test cells. The chart recorder analogue output was connected directly to an A-D card in a personal computer. It was found during the calibration process, that the instrument had a surprisingly linear response, even when the instrument display was off-scale.

The unmodified PID sampled at a rate of 300 mL min\(^{-1}\) via an internal fan. The flow through the detector head was made adjustable by sealing the loosely sealed internal fan to the head with hot melt glue and replacing the hollow exhaust bolt with a new bolt with a spigot. The laboratory vacuum was attached to the exhaust via a precision flow valve, and it was found that the flow through the detector could be precisely set over a wide range (nominally 50 to 300 mL min\(^{-1}\)). This was important for two reasons. Firstly, when the flow rate through the permeation cells was low, the flow to the PID had to be...
lower to ensure it did not sample room air. Secondly, air flowing past the PID inlet had the potential to affect the response of the PID. The response of the detector (with acetone) was found not to vary with flow through the PID and the flow from the GloveTest rig was found not to alter the flow into the PID.

SECTION B.2 DEVELOPMENT OF THE ADVANCED GLOVETEST RIG

The shortcomings of the prototype GloveTest rig included

- Poor detection limit due to difficulties in decontaminating the plumbing between runs
- A relatively high resistance to flow through the electrical solenoid values
- Heating of the solenoid blocks by the solenoid wiring
- "Spaghetti" wiring of the rig, decreasing reliability
- A slow computer and small screen, hindering real time processing and display of data
- Flexing of the cell clamping frame during tightening of the cell clamping bolts

These shortcomings were overcome in a complete rebuilding of the test rig.

Table 25 GloveTest rig evolution

<table>
<thead>
<tr>
<th>Feature</th>
<th>Prototype Rig</th>
<th>Advanced Rig</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Visual Basic 3 Professional</td>
<td>Same</td>
</tr>
<tr>
<td>Computer A-D</td>
<td>Generic 486 33 SX</td>
<td>Dell Pentium 133</td>
</tr>
<tr>
<td>PLC</td>
<td>Same</td>
<td>Same</td>
</tr>
<tr>
<td>Detector</td>
<td>HNU 101 PID (10.2 eV lamp)</td>
<td>HNU 101 PID (10.2 eV)</td>
</tr>
<tr>
<td>Cells</td>
<td>8 Griffith Large Cells</td>
<td>8 Griffith Large Cells</td>
</tr>
<tr>
<td></td>
<td>8 Griffith Small Cells</td>
<td>8 Griffith Large Cells Mk2</td>
</tr>
<tr>
<td></td>
<td>1 Mk1 Intermittent</td>
<td>8 Griffith Mk2 intermittent</td>
</tr>
<tr>
<td>Flow measurement</td>
<td>Honeywell 1 Lpm</td>
<td>Honeywell 10 Lpm</td>
</tr>
<tr>
<td>Flow Dilution</td>
<td>Dilution chamber</td>
<td>Increased flow rate</td>
</tr>
<tr>
<td>Pressure</td>
<td>None</td>
<td>Micro-manometer based on Sensym SCXL004DN pressure sensor</td>
</tr>
<tr>
<td>Temperature</td>
<td>Thermistor</td>
<td>Thermistor plus thermocouples</td>
</tr>
<tr>
<td>Vacuum</td>
<td>Polycarbonate lid, lab vacuum</td>
<td>Aluminium lid, Rotary vacuum pump</td>
</tr>
<tr>
<td>Oven</td>
<td>Option on standard trial</td>
<td>More configurable</td>
</tr>
<tr>
<td>Intermittent</td>
<td>Steel 8 cell frame</td>
<td>2 x Heavy Steel 4 cell frames</td>
</tr>
<tr>
<td>Frame</td>
<td>Wooden Baseboard</td>
<td>Modular – electricals and solenoids Detachable backplane</td>
</tr>
</tbody>
</table>

The test rig is shown schematically in Figure 25. Electrical connections are shown as single lines and gas flows as double lines.
The layout of the valves may be more easily understood with the aerial view of the hardware in Figure 190.

The main feature of the test rig is a high degree of automation while testing eight cells in sequence in a one-minute cycle, with no intervention once the challenge solvent is placed in each cell. The test rig is also capable of rapid re-configuration though software changes and quick connect fittings between most elements.

The test rig is designed to sequentially measure the chemical permeating each cell by diverting flow through each cell to a HNU P101 photoionisation detector with a 10.2 eV lamp (PID) sensor. Carrier Gas (high purity nitrogen) enters the test rig from a gas
regulator. The nitrogen flow can be stopped with a Cut-Off Solenoid Valve “sc” or Manual Ball Valve “b” to conserve nitrogen. The nitrogen pressurises the Inlet Manifold and then flows to the cells via Metering Valves “m” (Swagelock NUPRO B 224). The nitrogen supply pressure (90 kPa) is sufficient to ensure that flow though one cell does not affect the flow through another. The Cells 1 to 8 are clamped in a rigid steel frame, in a row, each with its own Metering Valve.

The exhaust from each cell is normally directed to waste by the Poppet Valves “p” operated pneumatically by solenoid valves “s”. These Poppet Valves are switched in sequence to allow the carrier gas from each cell to be tested by the PID sensor. The flow to the PID sensor is diverted just before each measurement, by the Flow Metering Diversion Solenoid and Poppet Valves “sf” and “pf” respectively, to a mass flow sensor (Honeywell AW5000), to measure the flow though the cell. This delay is not wasted as it allows the line from the cell to the Poppet Valve “pf” to be flushed and greatly reduces chemical exposure to the flow sensor. The whole collecting line from Solenoid Valve “sf” to the PID sensor and temperature sensor “t” is flushed with 5 Lmin⁻¹ nitrogen by solenoid “sf” before the start of a trial, and then as required.

Temperature of the carrier gas is measured by a temperature sensor “t” (National Semiconductor LM335Z), in the gas flowing past the PID sensor and the flow through the PID sensor is controlled by the Metering Valve “mp” connected to the laboratory vacuum. All cells are treated the same, except that flow rates through the cells are in approximate proportion to the exposed sample areas in each cell, to present the PID sensor with the same range of challenge chemical concentrations. Details of the Tain 4 channel thermocouple ampler were given in the body of the thesis.

Pressure was measured with a differential pressure meter⁸ based on differential pressure sensor (Sensym SCXL004DN, Sensym, Milpitas, Ca. http://www.sensym.com/sdx.htm 0-1000 Pa. Linearity: ± 0.5% full-scale output, Repeatability: ± 0.2% full-scale output). It has an analogue output for interfacing to a chart recorder or an A-D channel in the

⁸ The circuit was derived from a basic design by Sensym by Mr Werner Ehrsam and modified for the specific application. e-mail W.Ehrsam@mailbox.gu.edu.au.
GloveTest rig. It was checked against a precision manometer (Airflow Dynamics). The display was readable to 1 Pa.

The control solenoids are actuated by a Programmable Logic Control (PLC) card (Procon, Melbourne). The cards and software were initially driven by a generic 486SX IBM® compatible Personal Computer (PC), but later a Dell® 133 MHz Pentium® PC was used. Signals from the temperature sensor, mass flow sensor and PID are digitised by a generic 16 channel 12 bit analogue to digital converter card inside the PC.

![GloveTest hardware with eight Griffith Mk2 cells](image)

**Figure 191** GloveTest hardware with eight Griffith Mk2 cells

The plumbing has largely been confined to a base-plate (Figure 191), with electrical and electronic connections on a backplane than can be detached (Figure 192). Gas and vacuum connectors, gauges, extra needle valves and indicator lights were also attached to the backplane.
Figure 192 Rear of backplane with electrical and computer connections, PLC and gas and vacuum gauges

**B.2.1 GloveTest rig components**

The specifications for the components associated with the *GloveTest* rig are tabulated in Table 26.
Table 26 *GloveTest* rig components

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cells</strong></td>
<td>Griffith cell</td>
<td>All developed at Griffith University except the ASTM cell.</td>
</tr>
<tr>
<td></td>
<td>Griffith Small cell.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ASTM cell.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Griffith Intermittent exposure cell</td>
<td></td>
</tr>
<tr>
<td><strong>Carrier Gas</strong></td>
<td>High Purity Nitrogen</td>
<td>No IR interference from CO₂ and H₂O</td>
</tr>
<tr>
<td><strong>Carrier Gas Flow</strong></td>
<td>500 ± 10 mL min⁻¹</td>
<td>Higher than ASTM standard flow rates, but matches PID response</td>
</tr>
<tr>
<td><strong>Rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Experiment Time</strong></td>
<td>Normally 180 to 240 minutes</td>
<td>User defined up to 16 hours is possible</td>
</tr>
<tr>
<td><strong>Tubing</strong></td>
<td>6 mm OD Nylon</td>
<td>Pneumatic tubing 2000 kPa burst Pressure</td>
</tr>
<tr>
<td><strong>Connectors</strong></td>
<td>Quick Fit tubing connectors</td>
<td>Festo, Parker and SMC brands</td>
</tr>
<tr>
<td><strong>Flow Regulation</strong></td>
<td>Fine Metering Valves</td>
<td>Set before each experiment using GloveTest software</td>
</tr>
<tr>
<td></td>
<td>0.0005 CV Flow coefficient</td>
<td></td>
</tr>
<tr>
<td><strong>Flow Meter</strong></td>
<td>Done periodically using Buck and Gillian Calibrator</td>
<td>Stored as a file in software</td>
</tr>
<tr>
<td><strong>Calibration</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Flow Switching</strong></td>
<td>Solenoid and Poppet valves Festo</td>
<td>Controlled by PLC and software</td>
</tr>
<tr>
<td><strong>Cycle time for 8</strong></td>
<td>~ 120 seconds</td>
<td></td>
</tr>
<tr>
<td><strong>cells</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cycle time for one</strong></td>
<td>~ 15 seconds</td>
<td></td>
</tr>
<tr>
<td><strong>cell</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Flush time</strong></td>
<td>If used, 10 seconds @ 5 Lpm nitrogen</td>
<td>Flushes out the line between cells and PID</td>
</tr>
<tr>
<td><strong>Temperature Sensor</strong></td>
<td>LM 355 solid state temperature sensor</td>
<td>Output was 10 mV/°C, measured on output line of cell 1</td>
</tr>
<tr>
<td></td>
<td>Tain 4 channel T type thermocouple amplifier</td>
<td>Custom built by Tain Electronics, Melbourne. Read By 4 A-D channels. Fast logging and ~0.1 °C resolution.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermocouple instruments</td>
</tr>
<tr>
<td></td>
<td><strong>Solvents</strong></td>
<td>AR Grade: Toluene, Hexane, Acetone</td>
</tr>
<tr>
<td></td>
<td><strong>Solenoids</strong></td>
<td>12V regulated supply external source. Later, an unregulated plug pack.</td>
</tr>
<tr>
<td></td>
<td><strong>Flow meter</strong></td>
<td>10V regulated from PC off A/D card in PC</td>
</tr>
<tr>
<td></td>
<td><strong>PLC</strong></td>
<td>5V from PC off PLC output card in PC</td>
</tr>
<tr>
<td><strong>Flow Rate detector</strong></td>
<td>Honeywell mass flow sensors</td>
<td>Each cell’s flow rate was logged during the experiment</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
<td>HNU Photo ionisation detector</td>
<td>1-1000 ppm nominal range</td>
</tr>
<tr>
<td></td>
<td>Model PI 101</td>
<td></td>
</tr>
</tbody>
</table>

The items in Table 26 are discussed in more detail below. The permeation cells are presented in more detail in Section B.3.
Programmable Logic Controller (PLC)

The PLC used in the GloveTest rig is manufactured by ProCon Technology (Melbourne) and is controlled directly from the PC via software. The software configuration is explained in Appendix C. The PLC used has 16 controllable output devices of which 14 were used for this project.

A PLC board was selected in preference to a stand alone PLC as it more directly linked to the Personal Computer (PC) and allowed the integration of the PLC and the data-logging with an A-D board. Modifications to the code could be more rapidly achieved. The initial package purchased had eight output channels, a modified printer card that allowed bi-directional flow of information between the PLC and PC and some software and utilities.

![Figure 193 Eight Channel PLC (Procon)](image)

It was quickly discovered that more than eight channels would be needed to control flow to the eight cells, as it was desirable to:

- switch in an extra flow to flush the line between the cells and the detector
- switch the flow between the detector and a flow sensor
- automatically switch off the nitrogen flow at the end of a trial
- add extra lines for experimental cells

One choice was to purchase a second card and daisy chain it with the first card, but an economical sixteen-channel PLC card with a sufficient current capacity to switch the solenoids was chosen. This left spare capacity for adding extra cells or swapping channels on the PLC, if and when a solenoid failed.

Cell clamp

The initial cells that were developed for holding together the test cells each had their own clamp made from scrap aluminium from the faculty workshop. Ten were
manufactured in the faculty workshop for use in an undergraduate experiment to determine the BT and SSPR of gloves.

The cell clamp was redesigned when the Griffith Mk2 cell was developed to increase the rigidity and accommodate the extra height of the cells, including the Griffith Mk2 intermittent exposure cell. Holes in the frame were bored on a digitally positioned milling machine and the columns bored and faced on a lathe. This precision ensured a high degree of alignment (within 10 μm). Tests with a dial gauge (1 μ sensitivity) on a mechanically flat plate indicated that a bowing of the base of 50 μm (about the thickness of a human hair) occurred when the bolts clamping the cells were tightened.

Figure 194 Heavy Frame design

This bowing was enough that tightening one cell slightly loosened the other cells. The test rig design required rapid setup of the cells, so modifications to the frame were needed to avoid a complex sequence of tightening of the clamping bolts for each cell.
The clamping frame was lengthened to allow additional bolts to be added between each cell to minimise this bowing. This bowing was reduced to less than 1 μm with this arrangement, which did not noticeably affect the clamping of adjacent cells.

**Analogue to Digital Converter (A-D) card**

The initial plan was to purchase a single multimeter with an RS232 (serial) connection, to connect to a PC. For much the same price, a 16 channel 12 bit A-D converter card was purchased. This allowed a number of instruments or sensors with analogue outputs to be connected. As a result, a mass flow sensor was also purchased, to keep a continuous check on flow rates of the carrier gas. A temperature sensor to measure the temperature of the carrier gas as it left one of the cells (cell 1) was constructed. With 12 bits, the digitising resolution is 4096. Full scale from the HNU meter was about 3600. The A-D was supplied by ProCon Technology and was manufactured in Taiwan.

The specifications of the A-D are summarised in Table 27 below. The GloveTest rig uses three analogue inputs and these are 1, 2 and 3 respectively. Input 1 is the HNU solvent detector, Input 2 is the flow meter and Input 3 is the temperature sensor. The base address of the A-D was set to 170 Hex, with the option of 160 Hex settings in the GloveTest software. These settings are also changed by jumper switches on the card itself.
Table 27 A-D specifications

<table>
<thead>
<tr>
<th>Digital to Analogue (not used)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
</tr>
<tr>
<td>Output Channels</td>
</tr>
<tr>
<td>Output Voltages</td>
</tr>
<tr>
<td>Unipolar Output</td>
</tr>
<tr>
<td>Bipolar Output</td>
</tr>
<tr>
<td>Conversion Time</td>
</tr>
<tr>
<td>Output impedance</td>
</tr>
<tr>
<td>Accuracy</td>
</tr>
<tr>
<td>Temperature Coefficient</td>
</tr>
</tbody>
</table>

| Analogue to Digital
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
</tr>
<tr>
<td>Input Voltage range</td>
</tr>
<tr>
<td>Unipolar</td>
</tr>
<tr>
<td>Bipolar</td>
</tr>
<tr>
<td>Conversion time</td>
</tr>
<tr>
<td>Accuracy</td>
</tr>
<tr>
<td>Output Coding</td>
</tr>
<tr>
<td>Maximum input voltage</td>
</tr>
<tr>
<td>Channel Numbers</td>
</tr>
<tr>
<td>1. 16 channels : Single Ended Input</td>
</tr>
<tr>
<td>2. 8 Channels Differential Input</td>
</tr>
<tr>
<td>Temperature Coefficient</td>
</tr>
</tbody>
</table>

**Computer**

The initial design was to use a dedicated PLC controller. However, it rapidly became apparent that a vastly greater flexibility and cost effectiveness would be gained by using a dedicated PC as a PLC, data logger, and post processor. The computer used as the *GloveTest* rig controller was a generic brand 486 with a Chinese manufactured main board and *Intel 486-SX* microprocessor. The RAM memory consisted of 4 x 1 Mb SIMMS (30 pin) modules and a 250 Mb hard disk (Seagate IDE). There was no cache memory on the board. The primary use of the PC was to control the *GloveTest* rig and perform data analysis.

**B.2.2 Detectors**

Three detectors (PID, flow, and temperature) were used in the *GloveTest* rig and all were logged via the A-D and the data stored on disk. The detectors are described below:

**HNU 101 Photo-ionisation Detector (PID)**

The original PID as described in sub-section B.1.2 was used as the solvent detector, but with modifications to the flow through the ion chamber.
Honeywell Microbridge mass flow sensors

To ensure that flows through each cell did not vary, an economical Microbridge AW3000 mass flow sensor manufactured by Honeywell Limited was sourced.

Figure 195 Honeywell Microbridge AW3000 mass flow sensor

It has an operating flow rate from 50 mL min\(^{-1}\) to 1000 mL min\(^{-1}\) with an almost linear scale. The flow meter produces an output voltage proportional to the flow rate and direction. Typically, the output voltage is trimmed to be 5V at 1000 mL min\(^{-1}\).

The flow past the PID was indirectly measured by alternating the flow past the PID and a mass flow sensor with a solenoid valve thus avoiding excessive solvent exposure to the mass flow sensor. It also allowed high flushing flow rates in the collecting line when the flow switched past the PID. The mass flow sensor output was calibrated with a Buck Calibrator on the output of the flow passing the PID and the calibration curve stored as a file.

This sensor eventually failed through mishap and was replaced by a higher capacity AWM5000 (10 Lpm) sensor in the same range. The new sensor had linearising circuits, reducing the amount of linearising required in the calibration curve.

Figure 196 Honeywell Microbridge AWM5000 mass flow sensor

(From http://www.honeywell.com/sensing/prodinfo/massairflow/catalog/c15_79.pdf)
**Mass flow sensor calibration**

To calibrate the mass flow sensor for Nitrogen over a wide range of flows, bubble tubes were used, and the performance if the bubble tubes cross checked against each other. Three of the bubble tubes were electronic and one was manual.

**Table 28 Flow measurement devices**

<table>
<thead>
<tr>
<th>Bubble Tubes</th>
<th>Range (mL min⁻¹)</th>
<th>Calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gillian bubble tube</td>
<td>20 - 6,000</td>
<td>Calibration certificate</td>
</tr>
<tr>
<td>Gillian bubble tube</td>
<td>2,000 - 30,000</td>
<td>“99% accuracy” claimed</td>
</tr>
<tr>
<td>Buck bubble tube (model M5)</td>
<td>1 - 6,000</td>
<td>±0.5% repeatability claimed</td>
</tr>
<tr>
<td>SKC bubble tube (model 302)</td>
<td>100 - 4,000</td>
<td>SKC claim ±0.5%, NIST*</td>
</tr>
<tr>
<td>Honeywell AW3300</td>
<td>0.1 - 1,000</td>
<td>±1% repeatability claimed</td>
</tr>
<tr>
<td>Honeywell AW5102</td>
<td>1 - 10,000</td>
<td>±0.5% repeatability claimed</td>
</tr>
</tbody>
</table>

* NIST: US National Institute of Standards and Technology, The Calibration of Small Volumetric Laboratory Glassware

**Temperature sensor.**

A semiconductor temperature sensor (National Semiconductor LM335 precision temperature sensor) was mounted in a piece of clear tubing in the line coming from cell one and the temperature signal was fed to the A-D card.

![Figure 197 Temperature sensor and electronics](image)

A trim potentiometer adjusted the offset. It has an output of 10 mV/s/°K and very high precision. The sensor was calibrated against a certified thermometer (NATA) and was accurate to within ±0.1°C.

The developments with thermocouples are described in Chapter 9.

**SECTION B.3 PERMEATION CELLS**

Seven types of cell were used for the experiments:

- Griffith cell
- Griffith Small cell.
The exposed sample area of the continuous cells was an important determinant of the cell design. Small sample areas reduced sensitivity making nBT measurements difficult and large sample areas required a high flow rate to ensure that the concentration of permeant at the detector could be measured. Details of the dimensions for four cells are presented in Table 29.

**Table 29 Cell comparisons**

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Diameter (mm)</th>
<th>Area (cm²)</th>
<th>Flow required for same flow : area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Griffith cell</td>
<td>21.7</td>
<td>3.7</td>
<td>500</td>
</tr>
<tr>
<td>Griffith Small cell</td>
<td>9.5</td>
<td>0.71</td>
<td>96</td>
</tr>
<tr>
<td>ISO cell</td>
<td>25</td>
<td>4.9</td>
<td>664</td>
</tr>
<tr>
<td>ASTM cell*</td>
<td>44</td>
<td>15.2</td>
<td>2056</td>
</tr>
</tbody>
</table>

*B as used in this work

**B.3.1 Griffith Cell**

This cell is similar in design specifications to the ISO cell. The cell itself is constructed from brass with 1/8 BSP threaded tube connectors to take 6 mm OD tubing. The clamping tubes are stainless steel of grade #316 and the clamp tops are also constructed from brass. The diameter of the Griffith cell is 21.7 mm with an area of 370 mm². This compares well with the ISO cell with a diameter of 25 mm and an area of 491 mm². The Griffith cell is a more compact design than the ISO cell with the carrier gas input and output 180 degrees opposed and in the same plane as the base. The sample sits parallel to the base with the solvent on top under atmospheric pressure. A stainless steel tube is clamped on top of the sample to hold it in place and these forms a seal between the sample and solvent. This method of clamping has proved to be very effective as a solvent seal and is much simpler and quicker than the ISO cell. The ISO cell in comparison is much larger then the Griffith cell, it is bolted together with 4 bolt holes cut into each sample for construction. The ISO cell does not sit flat and has to be clamped into place. The Griffith cell is able to placed on a bench top and many can be placed close together where the ISO cell must be clamped in a stand because of the orientation of the carrier gas input and output ports.
**Design features of the Griffith cell**

The major features of the Griffith cell are:

- it is very quickly assembled and disassembled;
- it is small, using only 1 mL of (toxic) challenge chemicals;
- it is capable of being used on intact garments;
- samples are quickly prepared using a wad punch;
- samples may be taken from most areas of a garment, including the fingers of gloves;
- it has a fast response time from a lower dead volume (3.7 mL, compared to 100 mL for the ASTM cell);
- it can be adapted for use with solids (Fricker and Hardy, 1994) and gaseous challenge chemicals (with a sealed lid), though the ASTM cell too can be used with gaseous challenge chemicals;
- it is mechanically robust, as it was undamaged by 1 m drops onto the laboratory floor;
- it can be easily made in a small workshop on a metalworking lathe;
- it is less bulky than the ASTM cell and ideal for use if a number of cells are used together.

The Griffith cells were machined in 1992 with an old lathe with failing bearings. In 1997, the body of the Griffith cells were stamped with an identifying number and precise measurements with digital callipers (readability 10 μm) revealed that there was some variation in the dimensions of the cells. The Griffith Small cells, which were made several years later, were stamped with a letter. As the cells were of essentially the same design, the same code for the dimensions is used (Figure 200). The identifying code was recorded each time a cell was used.
The pictures and drawings of the cells have been duplicated in this Appendix to make the dimension code in Figure 200 more easily understood.
Appendix B GloveTest Rig, Cells and Accessories

Figure 200 Cell Dimension code, Griffith cells

Table 30 Dimensions of the Griffith cell

<table>
<thead>
<tr>
<th>Large Cell ID</th>
<th>A (mm)</th>
<th>B (mm)</th>
<th>C (mm)</th>
<th>D (mm)</th>
<th>E (mm)</th>
<th>F (mm)</th>
<th>Coll Area (cm²)</th>
<th>Variation from mean Area (%)</th>
<th>Coll Vol (cm³)</th>
<th>Variation from mean Vol (%)</th>
<th>Collecting Depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.04</td>
<td>20.83</td>
<td>3.36</td>
<td>5.00</td>
<td>17.51</td>
<td>3.408</td>
<td>0.1</td>
<td>0.7</td>
<td>-14.7</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>27.46</td>
<td>20.85</td>
<td>2.65</td>
<td>5.38</td>
<td>17.58</td>
<td>3.414</td>
<td>-0.1</td>
<td>0.6</td>
<td>-4.4</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>27.07</td>
<td>21.11</td>
<td>3.75</td>
<td>5.95</td>
<td>17.72</td>
<td>3.500</td>
<td>-2.6</td>
<td>0.4</td>
<td>30.7</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>26.38</td>
<td>21.28</td>
<td>2.88</td>
<td>4.57</td>
<td>17.53</td>
<td>3.557</td>
<td>-4.3</td>
<td>0.5</td>
<td>16.9</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>26.75</td>
<td>21.00</td>
<td>4.63</td>
<td>7.18</td>
<td>17.69</td>
<td>3.464</td>
<td>-1.5</td>
<td>0.5</td>
<td>16.9</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>26.92</td>
<td>20.73</td>
<td>4.09</td>
<td>6.75</td>
<td>17.83</td>
<td>3.375</td>
<td>1.1</td>
<td>0.7</td>
<td>-22.3</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>26.94</td>
<td>21.20</td>
<td>3.55</td>
<td>6.30</td>
<td>17.44</td>
<td>3.530</td>
<td>-3.5</td>
<td>0.7</td>
<td>-23.7</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>26.74</td>
<td>20.80</td>
<td>3.35</td>
<td>5.50</td>
<td>17.63</td>
<td>3.398</td>
<td>0.4</td>
<td>0.6</td>
<td>2.3</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>27.12</td>
<td>21.33</td>
<td>4.16</td>
<td>7.06</td>
<td>17.53</td>
<td>3.573</td>
<td>-4.8</td>
<td>0.6</td>
<td>-1.9</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>26.94</td>
<td>21.01</td>
<td>3.60</td>
<td>6.10</td>
<td>17.61</td>
<td>3.41</td>
<td>0.60</td>
<td>1.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>0.30</td>
<td>0.22</td>
<td>0.63</td>
<td>0.85</td>
<td>0.66</td>
<td>0.12</td>
<td>0.07</td>
<td>0.11</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE %</td>
<td>1.11</td>
<td>1.07</td>
<td>17.50</td>
<td>13.97</td>
<td>13.29</td>
<td>0.70</td>
<td>2.17</td>
<td>18.76</td>
<td>41.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is evident from the estimates of Standard Error (SE) that machined dimensions involving diameters varied by about 1%, but dimensions involving depth varied more (13 to 17%). This may be attributed to the lack of precise instructions to the machinist and the quality of the lathe.

**B.3.2 Griffith Small Cell**

This cell is a scaled down version of the Griffith cell, with a diameter of 9.5 mm and an effective exposure area of 71 mm². It uses the exact same clamping system as the Griffith cell. The size of the cell permitted a large number of biopsies to be cut from a single glove and so a higher degree of precision of the overall performance of the glove could be attained. The smaller cells are also better aligned with the full-scale response of the HNU photo-ionisation detector, but the smaller area limited the sensitivity of the cell to breakthrough of the test chemical.
The dimensions of the Griffith Small cells, stamped A-R are given in Table 31.

### Table 31 Dimensions of the Griffith Small cell

<table>
<thead>
<tr>
<th>Griffith Small cell ID</th>
<th>A (mm)</th>
<th>B (mm)</th>
<th>C (mm)</th>
<th>D (mm)</th>
<th>E (mm)</th>
<th>F (mm)</th>
<th>Coll Area cm²</th>
<th>Variation from mean Area (%)</th>
<th>Coll Vol (cm³)</th>
<th>Variation from mean Vol (%)</th>
<th>Collecting Depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.22</td>
<td>9.49</td>
<td>2.07</td>
<td>3.00</td>
<td>5.69</td>
<td></td>
<td>0.707</td>
<td>4.4</td>
<td>0.055</td>
<td>54.7</td>
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<td></td>
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<td>0.093</td>
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<td></td>
<td>0.722</td>
<td>2.4</td>
<td>0.106</td>
<td>12.2</td>
<td>0.90</td>
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<td>1.75</td>
<td>3.74</td>
<td>5.91</td>
<td></td>
<td>0.74</td>
<td>0.12</td>
<td>0.03</td>
<td>0.33</td>
<td>0.91</td>
</tr>
<tr>
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<td>0.23</td>
<td>0.44</td>
<td>0.20</td>
<td>0.19</td>
<td>0.04</td>
<td>0.03</td>
<td>0.33</td>
<td>0.33</td>
<td>0.91</td>
</tr>
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<td>2.49</td>
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<td>11.67</td>
<td>6.98</td>
<td>3.22</td>
<td>5.00</td>
<td>28.8</td>
<td>36.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The machining errors for the Griffith Small cell are of the same order as for the Griffith Cell, but greater care was taken in machining with the depth dimensions.

Figure 202 shows the Griffith Small cell and the Griffith cell side by side with the samples, to give an indication of relative size.
B.3.3 ASTM F739 Cell

The glass ASTM F739 cell was constructed by Labglass Pty Ltd, a local company, to ASTM specifications (ASTM F739, 1986). The ASTM specification had a glass stirrer, but this was not used, as there would have been adequate turbulent mixing at the flow rates used.

B.3.4 Griffith Mk2 Cell

This cell is discussed in detail in Chapter 4 and additional cell validation details are given in Appendix E.

B.3.5 Griffith Mk1 Intermittent exposure cell

An automated intermittent exposure cell was designed and constructed to mimic actual workplace exposure by a wetting and drying effect on the glove sample. The cell uses an inverted Griffith cell that sits on top of the intermittent exposure base. The cell is connected into the prototype GloveTest Rig but with a special clamp, next to the cell 8 position and works as any other cell, but with additional pneumatic controls. The intermittent exposure base consists of a solvent reservoir, gas input, output jets and drying input. The exposure of the cell is regulated through software and can be set to any time period, though 15 minutes was used in most of the trials. After the exposure, the sample is dried by two methods: natural drying or forced air (waste carrier gas) drying. To expose the glove sample, compressed air is pumped into the reservoir and this forces solvent through jets onto the sample. The solvent is able to drain back into the reservoir on removal of the supply air, to be used for subsequent exposures when the compressed air is turned on again.
**B.3.6 Prototype Griffith Mk2 Intermittent exposure cells**

This was a development from the Griffith Mk1 Intermittent exposure cell and the Griffith Mk2 cell. Three examples of the prototypes are presented to demonstrate alternatives considered during the development of the Griffith Mk2 Intermittent exposure cell.

An intermittent version of the Griffith Small cell was rejected because the small size of the components would have made machining difficult and miniature nozzles to wet the test sample were difficult to source. In addition, the experience with the continuous cells indicated that insufficient sensitivity was obtained with the Griffith Small cell. It would however, be possible to adapt the Griffith Mk2 Intermittent exposure cell design to a miniature version.

![Prototype intermittent exposure cell based on a Griffith Small cell design](image)

**Figure 203 Prototype intermittent exposure cell based on a Griffith Small cell design**

The designs in Figure 204, based on the Griffith Mk2 cell were also considered, but the smallest solid cone commercially available nozzle was too large and an alternate design using an insert was too complex.
 SECTION B.4 ACCESSORIES

B.4.1 Sampling Bags

Flushing and filling of sampling bags

It was thought that by making the preparation of the Tedlar sampling bags with a predetermined amount of nitrogen and making the flushing of the bags between calibration points repeatable and automated, the process could be made more precise and quicker. There was some concern that the Tedlar bags could become over-inflated or the mass flow controller could be pressurised and fail, so the filling mechanism and software were designed to minimise this possibility. This was achieved by making the failsafe connection of the bag to a vacuum as shown in Figure 205. The ports "NO" are normally open and the ports "NC" are normally closed. The Control Solenoids for the two poppet valves “A” and “B” were selected from spare solenoids on the GloveTest rig, nominally solenoids 9 and 10 and the nitrogen supply was from a metering valve on the nitrogen supply manifold.
The operation of the bag fill mechanism can be seen with the truth table in Table 32. The ticks indicate flow through the indicated port. In the case of a computer or power failure, it failsafe connection to the vacuum rather than the gas line was required.

**Table 32 Bag fill truth table**

<table>
<thead>
<tr>
<th>Port on poppet valve</th>
<th>Flush bag/Fill bag</th>
<th>Empty bag/Fail Safe</th>
<th>End Fill/Set Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Transducer</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Tedlar Bag</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Vacuum</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

It was found that the regulation of the nitrogen flow with a precision needle valve produced a very steady slow and the error in measuring the flow during the fill or just the diverted flow to fill the bag was less than 1%. On completion of filling of a bag, the nitrogen flow was directed to the flow transducer from the bag, effectively sealing the bag.

Code was written to partially fill the bag five times with high purity nitrogen before emptying it by switching the flow to the vacuum. On the sixth fill, the bag was filled to 4 L of nitrogen or 80% of its rated capacity. Very precise filling was effected by calculating the fill times from the flow rate through the mass flow transducer and then switching the flow to the bag for the exact duration of the fill. All timing and switching was achieved under software control. It is estimated that the accuracy and precision of the timing is of the order of 0.01 seconds. The usual fill rate was at 1000 mL min\(^{-1}\), chosen as the Gillian bubble tube used to calibrate the mass flow transducer was certified at this flow rate. This produced a fill time of 4 minutes, making any timing error insignificant.
Precise injection of solvent into the sampling bags

It was difficult to hold the Tedlar bag, micro-syringe and plunger with two hands, so a jig was developed to hold the injection port of the bag, freeing both hands to use the micro-syringe. This simple jig, made from wood and secured with a wing nut resulted in a greater precision of injection of the solvent into the bag. The solvent was left to evaporate for about one minute and then the bag kneaded gently for about 30 seconds to minimise heating of the bag with ones' hands to mix the nitrogen and solvent vapour in the bag. The jig with a 5 L SKC Tedlar bag and 10 μL SGE micro-syringe is shown in Figure 206.

Figure 206 Sampling Bag injection jig

Trials were performed to remove air bubbles from the syringe by rapid pumping (a technique favoured by gas chromatography users) and by filling from an inverted vial of solvent through a septum advocated by Perkins (1997). No difference could be detected between the techniques, using 10 μL (100 g) of water weighed on a Sartorius 5M microbalance that had a resolution of ±1 μg.

The wait between the filling of the bag with nitrogen and its use to calibrate the PID proved to be important. The Tedlar bag walls retain a memory of its past use, and delays of a few minutes in using a bag allowed significant amounts of solvent to be desorbed from the bag walls. Knowing that solvents like acetone were polar and that the Tedlar (polyvinyl fluoride) was also polar lead to an investigation of how much and how far the acetone permeated the walls of the Tedlar bag. A non-polar solvent, n-hexane, was used as a control. See Chapter 8 for details of this experiment.
Emptying of the Tedlar sample bag atmosphere

The Tedlar bag was placed in a bucket and connected to 6 mm tubing passing through the side of the bucket. On the outside of the bucket, the flow passed through the mass flow transducer and the flow was sampled by the PID. Soap bubble tests had shown the seal between the bucket and the tubing to be airtight. A digital micro-manometer was also attached to the bucket and its output read by the A-D card. An airtight lid was placed on the bucket and a rubber bung placed in a large hole in the lid. The large hole permitted any displaced air to leave the bucket without squeezing the bag. Finally, a plug was placed in a piece of tubing in the lid of the bucket, sealing the bucket. This final plug had proved essential, as it was difficult to insert the rubber bung without pressing down on the lid of the bucket. Once the bucket was sealed a metered flow of air or nitrogen was introduced into the bucket, and logging and display of the PID, pressure meter and flow transducer started. The flow out of the bag was controlled by the flow of the displacing gas into the bucket.

As the bag was squeezed, the pressure in the bucket gradually rose until the bag was near empty. At this point the pressure inside the bucket increased and at around 600 Pa the experiment was terminated either manually, or automatically by the software using a pre-set trigger pressure.
The flow from the bucket was punctuated by small increases in flow that coincided with crinkling noses from the bag collapsing. It was observed that as the bag collapsed, a surface with many facets developed. The crinkling noise was attributed to ridges collapsing and the volume of the bag suddenly decreasing. These flow fluctuations made no observable difference to the PID level.

**B.4.2 Vacuum Drying Oven**

To enable a fast efficient method of drying the *GloveTest* cells between trials and connecting tubing, a very cheap and effective vacuum oven was developed. It was based on the only flat based, circular frypan available (Kambrook, Australia). This was purchased without a lid, but a similar sized sheet of polycarbonate plastic, thickness 12 mm, purchased. Polycarbonate is very chemical resistant, impact resistant and sufficiently temperature resistant. It is used for riot shields. A circular O-ring groove was machined in a lid cut from the sheet and a spigot attached to this lid for connection to a vacuum line. The temperature regulation at 60°C was ±0.1°C. The seals in the pneumatic connectors on the cells were rated to 60°C.

![Figure 208 Vacuum oven](image)

A spacer was added between the lid and the bottom of the pan to reduce the warping of both oven base and lid caused by the vacuum, after repeated usage. The temperature regulator failed at one stage, causing the spacer to be driven into the polycarbonate lid. For reasons of safety, the lid was replaced with an aluminium lid with small polycarbonate windows.

**B.4.3 Power Supply**

A regulated power supply was constructed to ensure the correct voltage supplied the solenoids but there were a number of failures of the relays on the PLC board, which may have been related to the large current capacity of the power supply. It was eventually replaced with a cheap "plug pack" power supply, eliminating the burnout of relays on the PLC board.
APPENDIX C. GLOVETEST SOFTWARE

The GloveTest software that controlled the GloveTest rig, and logged and displayed data evolved through a number of stages. The prototype software was developed under the direction of the author. It was significantly changed and enhanced during this project.

SECTION C.1 PROTOTYPE GLOVETEST SOFTWARE

The Developer’s version of Visual Basic (VB Pro v3.0) was chosen to develop the control language for the test rig. Visual Basic is a powerful object orientated language that forces structure and modularisation of the programming code. It has been estimated that 70% of the effort in programming is in developing the visual or human interface. With Visual Basic, the traditional programming conventions are reversed, and the starting point is the visual interface. The programming code is then written to connect the various elements, including those such as data input windows, data displays in numeric or graphical form and Input - Output (I/O) devices such as the PLC, A-D and printers. The work paid dividends in the degree of automation and sophistication in the operational test rig.

A version of Visual Basic, Visual Basic for Applications, is now the macro programming language in all the Microsoft Office applications such as Word and Excel. The learning associated with GloveTest software development was applied to the implementation of numeric models with Visual Basic for Applications in Excel.

SECTION C.2 GLOVETEST SOFTWARE

The GloveTest control program regulated the sequencing of the flow through the cells past the PID; measured the flow, temperature and solvent concentration in the collection medium through each cell in a cycle; linearised the response of the sensors; displayed all the data graphically and stored it as computer files for calculation of Breakthrough Times, Steady State Permeation Rates and any other permeation indices programmed into the code.

The following sections outlines the “GloveTest” control code. It is described from the point of view of the user in the first section “Menu Selections” and then for the programmer, in terms of the files. All the code for the prototype GloveTest rig was written by Mr Fraser Smith during the Worksafe Australia funded project, but it was subsequently checked, revised and greatly expanded upon by the author.
C.2.1 Overview of Software

The software was written as seven major “forms” and had three procedural forms. The seven major forms were:

- Glove1
- Glove2
- Glove3
- Comment
- About
- Analysis
- Flowcal
- STD

A brief description of each form is given below:

Glove1: the major form of the software, where most of the glove testing routines were located.
Glove2: for the testing of the flow rates through each cell and their adjustment before starting the experiment.
Glove3: for the setting of the cell which was "on" or "off" during a trial.
Comment: used to put comments onto the data file like glove type, position, solvent, and any other annotation. These comments were stored on the file header.
Analysis: used to post process the data, which was gathered by the system. This was used before or after a trial.
Flowcal: for the calibration of the flow meter
STD: for the experiment comparing the ASTM cell and the Griffith cells.
About: This was a small “lead in” program which contained some information about the software and the programmers.

A more compact form of the code would have used arrays, but changing the code was not justified, as the program size was a minor issue.

C.2.2 Global Functions and Procedures

To allow information to be used in all modules, a number of global (cf. local) functions and procedures were developed.

a_dconv(channel) This function performs analogue to digital (A-D) conversions and is a modified version of that supplied
with the card. The channel number is passed to the
function and the corresponding digital conversion is
returned.

**Flow(a())**

This function returns the flow meter reading in mL min⁻¹.
The variable “a()” is an array containing the coefficient of
the polynomial calibration curve.

**Flowvalve (solnumber)**

This function is used to turn on the solenoids required for
a flow measurement to take place.

**one_sol_on (sol)**

This function returns the string value required to turn any
one solenoid on.

**Timedelay: (deltime)**

This function is a wait timer in seconds, where the
variable deltime is the required wait time. This was
modified to account for resetting of timers at midnight.

A number of global variables such as file names and the elapsed experiment time were
also defined.

**C.2.3 Menu Selections**

The hierarchical structure of the menus as they appear on the computer screen is shown
in Figure 209. The most important items are in shaded boxes with heavy borders and the
least important in plain boxes.

![GloveTest Menus](image)

**Figure 209 GloveTest Menus**

An example of the *GloveTest* screen is shown in Figure 210. The menus can be seen
along the top.
The function of the sub-menus and each menu are:

**Menu: Experiment**

This is the main menu for performing trials and analysing the data. The function of each sub-menu is described below.

- **Start**
  
  This menu starts the main experiment.

- **Cell Validation**
  
  This menu was specifically designed for running validation trials with the ASTM cell. The menu was largely outdated with the use of a better flow-meter capable of taking the flows from all the cells used, and a better computer (Dell Pentium 133) that could easily display eight graphs on its larger (17") screen.

- **Analysis**
  
  The Analysis menu was developed to reproducibly fit mathematically derived lines to those that had previously been fitted by eye. A number of additional indices of glove permeation were also developed. The analysis package integrates and differentiates the open loop permeation curve for each cell, shows
the data graphically, fits best fit polynomials to the curves to reduce the effects of signal noise and calculates the indices.

**Diagnostics**
This is a general purpose "scratch" area where code was rapidly developed for testing a particular idea. Numerous snippets of code could be safely tested here without corrupting the standard code. The code to log and plot the effect of flow on permeation rate resides here.

**Menu: Options**
The options menu allowed choice of display of various groups of controls and some small procedures.

**Graph**
Vestigial code to permit the display of eight permeation graphs. This was no longer used when a larger monitor was used and all eight graphs could be displayed simultaneously during data acquisition.

**Flush**
This allows either the collecting line from the cell solenoids or the cells themselves to be flushed. This is particularly useful before a trial to ensure that the channels are all free from contamination. Flushes are also built into the normal operations and configurable to line flush after a predetermined number of cells for a predetermined period (seconds)

**Show Solenoids**
This allows the display or hiding of a large box showing the status of all the solenoids plus other transitory information in small graphs and boxes.

**Show Measurements**
This allows the display or hiding of graphical indicators of the output of the transducers (PID, Flow, Temperature and Pressure)

**Show Changes**
This allows the display or hiding of a scratchpad and controls that allowed notes to be stored or reviewed when changes were made to the program.

**Menu: Settings**
This allows the *GloveTest* configuration to be modified.

**Cell Flows**
This menu runs a module to set the flows through the cells.

**Cell Settings**
This permits the use of cells to be preselected, permitting any combination of cells to be used.
Program Settings  The base address of the PLC and A-D card is set here. Personal preferences on the screen colour of the graphs can also be set.

Menu: Help
About  Displayed a box with details of the program and its version.
Help  A comprehensive help program was planned, but the continual changes in the program made any attempts out of date. A help file was not necessary for running the program.

Menu: FTIR
FTIR Control  This displayed a box with controls to operate a Perkin Elmer 2000 FTIR. This included a detailed status report of the FTIR settings, initialisation, background spectra, data acquisition and features like naming of peaks and placing of grids on spectra. The code was based on the Perkin Elmer "Obey" code. It also had a button to hide the box to reduce clutter.
Initialise  This did the same as the Initialise selection in the FTIR Control, without having to show the FTIR Control box.

Menu: Calibration
HNU  The PID is calibrated with a known amount of solvent in a known volume of nitrogen in a Tedlar sampling bag. The code allows a Tedlar bag (SKC) to be flushed (five times) and then be filled to an exact volume for a known time (with millisecond accuracy) at a set flow rate from one of the metering valves. Typically, 1 Lpm for 4 min gave a very accurate and precise volume in the Tedlar bag. A precise amount of solvent (microlitres) is injected into the bag, allowing a calibration curve to be constructed. It was found more convenient for the calibration curves to be applied with a formula on an Excel spreadsheet, as scale changes of the PID had to be considered, and backgrounds subtracted.
Flow  This allows flows though cells to be checked and adjusted and displayed.
SECTION C.3 PROGRAMMING STRUCTURE

The structure of the *GloveTest* control program is shown in Figure 211 below. The more important modules have heavy boxes. Support and housekeeping modules have light boxes.

![GloveTest Program Modules](image)

**Figure 211 GloveTest Program Modules**

It is similar to the Menu structure, except that some of the items cover a number of menu items and some of the modules such as “Comments” are used in a number of parts of the program. There are two types of computer files shown above. The first are FORMS e.g. *glove1.frm*, which are the main programming module in Visual Basic. This is the building block of Visual Basic, and allows the interface to the user to be rapidly constructed. Visual Basic greatly reduces the time for this to be constructed using timers, scroll bars, moving bars, graphical displays and the like, each with a menu of attributes to set up its appearance. Code is written for each form to link these elements and the rest of the program. The other type above are BASIC program elements such as *glove11.bas*, which is Visual Basic code to enable the forms to operate together and set up the interface with the outside world. Not shown are DLLs (Dynamic Library Links), VBX’s (Visual Basic Extensions code) nor the Visual Basic environment itself.

The brief description below of the more important modules complements the Menu description above.
Forms

Main Module  This is the main form to show the Menu and control the standard experiment.

Data Analysis  This did the curve fitting and calculated the various indices for each cell.

Photo-ionisation Detector  This timed the filling of the Tedlar bag with a set amount of nitrogen and stored the output of the photo-ionisation detector with an entered microlitre injection of solvent into the Tedlar bag. From this data, a calibration curve was calculated.

Flow  Checking and calibration of the flow transducer

Cell Validation  Cross calibration of the cells with the Standard ASTM cell

SECTION C.4 GLOVETEST CODE STATISTICS

Project Analyzer 3.0.04 (16-bit, VBShop http://www.helsinki.fi/~salste/vb.html) was used to analyse the GloveTest code. Approximately a quarter the code was written by the author, a quarter by Mr Fraser Smith (Bromwich et al., 1997) for the prototype GloveTest rig, and half was propriety code from the Perkin Elmer "Obey" extensions to Visual Basic for use with the Perkin Elmer S2000 FTIR. The details of the FTIR code and interface to the GloveTest software using the Obey code have not been given.

Project: GLOVETST.MAK

Project created in Visual Basic 3.0

Files

Files: 82
DLL files: 15
VBX and OCX files: 18

Forms and controls

Forms: 22 (max 230)
Controls: 593

Procedures

Procedures: 1279
Procedures, Basic: 790
Procedures, DLL: 489
Procedures, Global: 844
Procedures, Private: 435
Subs: 610
Functions: 669
Procedures + modules + forms: 1312 (max 5200)

**Variables and constants**

Total variables and constants: 4088
Global and module-level variables and constants: 1728
- Global variables: 157
- Global constants: 901
- Module-level variables: 168
- Module-level constants: 502
Procedure-level variables and constants: 2360
- Procedure-level constants: 155
- Procedure-level variables: 1513
- Procedure parameters: 692

**Code size**

Lines of code: 32827
Bytes of code: 1252 kb
Lines of code per module: 994
Bytes of code per module: 37.9 kb
Lines of code per procedure: 41
Bytes of code per procedure: 1.6 kb
APPENDIX D. STATISTICAL METHODS

SECTION D.1 SAMPLE SIZE WHEN COMPARING TWO MEANS

The following approach was taken from Kirkwood (1988). The required sample size for each group when comparing two means is

\[ n = \frac{(u + \nu)^2(\sigma_1^2 + \sigma_2^2)}{(\mu_1 - \mu_2)^2} \]

.................................................. Equation 30 Sample size

where

- \( n \) = number of samples (tests on gloves) in each group
- \( u \) = one sided percentage point of the normal distribution corresponding to (100% - Power)
  e.g. if Power = 80% then \( u = 0.84 \), from tables
- \( \nu \) = percentage point of the normal distribution corresponding to the (two sided) significance level
  e.g. if significance level = 5% (\( \alpha = 0.05 \)) then \( \nu = 1.96 \), from tables
- \( \sigma_i \) = standard deviation of population \( i \)
- \( \mu_i \) = mean of group \( i \)

For these tests, the standard deviation of the group is taken as the same as the standard deviation of the population.

SECTION D.2 MEDIAN SPIKE FILTER

D.2.1 Introduction

A novel method of removing noise from digitised signals was developed using a running median value of a signal to remove spikes. Though simple, it can eliminate the spike without damping the signal, but return the true value for a monotonically increasing or decreasing signal.

Noisy signals can be filtered with low-pass electronic filters or by digital signal processing to retrieve the underlying true signal. Noise in signals produces poorer estimates of detection limits, as the detection limit of an analytical technique is usually determined in terms of detecting a non-zero signal in a background of instrument noise. The more the noise, the greater the detection limit.
The rate of chemical permeation through a membrane by simple Fickian diffusion increases monotonically, to asymptote at a Steady State Permeation Rate. Even if there is strong interaction between the test chemical and a CPC sample, the initial permeation can still be expected to increase monotonically. If a spiky noise signal is superimposed on an open loop permeation curve, then a significant overestimate of the true detection limit would be made, as the true trend would be very obvious on a graph of the detector output.

Random spikes comprising less than 10% of the number of data points were detected in the processing of the output from the PID. A simple method has been developed to remove the spikes from the signal.

**D.2.2 Theory of Median Spike Filter**

The median of an odd number of monotonically increasing numbers is the number in the middle. If the signal is 2 and the numbers each side of it are 1 and 3, the series is 1, 2, 3 and the median is 2, the true value of the signal. If a spike one unit wide (say 10) lands on any of the values, then the series becomes 10, 2, 3 or 1, 10, 3 or 1, 2, 10. The filter returns 3, 3, or 2, rejecting the spike and giving a correct or near correct value. There is a slight bias when the spike occurs before the middle of the filter.

If the values in a sequence of M samples varies between 1 and N, then the average difference between the numbers is N/M. If there are S unit width spikes, and S<<M (so than successive spikes are improbable), then the sequence is skewed by S.N/M. The approach could be extended to account for occasional successive spikes, and the mean height of the spikes would have to be known to calculate the error. Alternatively, the width of the running mean could be extended, to ensure rejection of two successive spikes or a spike two numbers wide. A spike could be taken to be a value much greater than N/M.

**D.2.3 Experimental**

Two trials were made using the Griffith cell challenging reference neoprene with acetone. The noisiest curve was processed using the median spike filter with windows three and five data points wide over about 1000 data points. Only the initial permeation curves were examined.
D.2.4 Results and Discussion

Figure 212 Initial permeation, acetone and reference neoprene, two trials

The spikes evident in the two trials shown in Figure 212 were a matter of concern as they limited the detection limit, even when the downward trend before the addition of the acetone was compensated for. The required ASTM "Normalised Breakthrough Time" required the detection of $0.1 \mu g \text{ cm}^{-2} \text{min}^{-1}$, and it is debatable whether a permeation rate as low as this could be detected with spikes in the data.

Using a median filter with a window three or five points wide, monotonically increasing or decreasing data return the centre point. If a spike is present it is discarded by the filter, and the next best estimate returned, as the median just ranks the data and selects the centre point. Unlike a running average, the filter's response is not damped - it just rejects fast spikes, so long as the spikes are shorter than half the window. It is effectively a special case of a low pass filter.
The graph in Figure 213 shows the effect of windows 3 and 5 datum points wide used to filter the spikes from the data. The filtered curves have been offset for clarity by a factor of 3 and 9 respectively to offset the curves on the logarithmic permeation scale. The filtered data produced almost identical curves, with minor differences when fluctuations occurred over successive datum points. In this case, there was little advantage gained in using a five point moving median.

**D.2.5 Conclusions**

The median spike filter appears to be a valid method of eliminating short, sharp spikes in an otherwise "clean" signal. Unlike a running average, it tends to follow rather than dampen a trend. The rejection of the noise in the signal permits a smaller background noise signal to be estimated, resulting in a lower analytic detection limit.
APPENDIX E. VALIDATION OF GRIFFITH MK2 CELL

This Appendix details the validation experiments that demonstrated that the Griffith Mk2 cell was equivalent to the ASTM F739-1996 cell. The detailed permeation data is presented, along with a discussion of the statistical approaches to determine the acceptance limits.

SECTION E.1 NORMALISED BREAKTHROUGH TIME

Three trials (D, E and F) were performed to determine the nBT for the Griffith Mk2 cell. An unusually elevated background was noted prior to the addition of acetone. The reason for this elevation was investigated. The permeation curves from these three runs and the ASTM nBT acceptance limits are shown in Figure 214. The permeation rate scale is logarithmic to show the early detail.

![Figure 214 Griffith MK2 cell nBT, acetone on ASTM neoprene](image)

Trial D appears to have a lower nBT than the other two runs. As the trial is otherwise normal, it is likely that the early breakthrough was related to a weak point in the sample. The weights of the samples were 316.550, 316.885 and 319.499 μg, indicating little variation in thickness. The samples were taken next to each other from a 400 μm thick sheet of reference neoprene.
**E.1.1 O-Ring Degradation during nBT Trials**

Though the nBT values were within the ASTM acceptance limits, the erratic permeation in Trials E and F was likely to be due to a degraded O-ring in the seal between the PID lamp and the PID ion chamber. Details of the three trials follow.

**Trial D:** A normal trial, but the background was noted to be higher than normal. This was only evident on the most sensitive scale (50 ppm on the PID).

**Trial E:** Before Trial E, stripping the PID detector revealed that the O-ring between the lamp and the ion chamber had deteriorated, and there were some flecks of the O-ring material on the Teflon ion chamber body.

**Trial F:** Before Trial F, the detector lamp, ion chamber and front enclosure were baked in the vacuum oven for 15 minutes at 60 °C. Only the ion chamber was baked (with its O-ring) before Trial E. Both attempts at decontamination actually increased the background and it was noted that the O-ring had actually broken in one place and was falling apart. A replacement O-ring was not available at the time.

The degraded O-ring could have affected the performance of the detector in two ways:

**Leakage of room air into the PID flow.**

As the room air produces an erratic and produced a much higher response than the high purity nitrogen (spiking to full scale), a leakage of room air this would add noise but tend to increase rather than decrease the signal. However, the response at high concentration would also decrease. The effect could be expected to be small, as the flows and pressure drops would be low near the O-ring. Thus leakage of room air was not thought to cause the erratic permeation below 0.1 μg cm⁻² min⁻¹.

**O-ring as a source of contamination**

The broken O-ring had many fissures that trap solvent from the prior trial and act as a low-level source during the subsequent trial. This was expected to be the main source of background noise that dropped on replacement of the O-ring. It is possible that the extended use of the PID lamp resulted in UV degradation of the O-ring.

**E.1.2 Tabular nBT Results**

Four earlier nBT measurements were made for the Griffith cell and three for the Griffith MK2 cell, before the PID O-ring failed. The data are tabulated in Table 33.
Table 33 Normalised breakthrough times

<table>
<thead>
<tr>
<th>Cell</th>
<th>nBT</th>
<th>trial</th>
<th>Mean</th>
<th>SD</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Griffith</td>
<td>9.5</td>
<td>10.2</td>
<td>10.3</td>
<td>10.6</td>
<td>10.2</td>
</tr>
<tr>
<td>Griffith Mk2</td>
<td>7.7</td>
<td>9.6</td>
<td>9.4</td>
<td>8.9</td>
<td>11.8</td>
</tr>
</tbody>
</table>

SECTION E.2  STEADY STATE PERMEATION RATE

E.2.1  Tabular SSPR Results

Table 34 shows the Steady State Permeation Rates for the 16 tests in 2 runs. The data is ordered by cell type, and the SSPR is based on seven measurements.

Table 34 Steady State Permeation Rates, Griffith cell and Griffith Mk2 cells

<table>
<thead>
<tr>
<th>Trial</th>
<th>Cell</th>
<th>Cell ID</th>
<th>SSPR</th>
<th>SD</th>
<th>n</th>
<th>CV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Griffith Mk2</td>
<td>2</td>
<td>217.0</td>
<td>3.9</td>
<td>7</td>
<td>1.81</td>
</tr>
<tr>
<td>1</td>
<td>Griffith Mk2</td>
<td>4</td>
<td>214.8</td>
<td>1.7</td>
<td>7</td>
<td>0.79</td>
</tr>
<tr>
<td>1</td>
<td>Griffith Mk2</td>
<td>6</td>
<td>218.2</td>
<td>7.6</td>
<td>7</td>
<td>3.47</td>
</tr>
<tr>
<td>1</td>
<td>Griffith Mk2</td>
<td>8</td>
<td>221.3</td>
<td>4.6</td>
<td>7</td>
<td>2.08</td>
</tr>
<tr>
<td>2</td>
<td>Griffith Mk2</td>
<td>10</td>
<td>215.9</td>
<td>0.9</td>
<td>7</td>
<td>0.43</td>
</tr>
<tr>
<td>2</td>
<td>Griffith Mk2</td>
<td>12</td>
<td>215.7</td>
<td>0.9</td>
<td>7</td>
<td>0.43</td>
</tr>
<tr>
<td>2</td>
<td>Griffith Mk2</td>
<td>14</td>
<td>207.1</td>
<td>1.0</td>
<td>7</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>Griffith Mk2</td>
<td>16</td>
<td>213.3</td>
<td>0.9</td>
<td>7</td>
<td>0.43</td>
</tr>
<tr>
<td>1</td>
<td>Griffith</td>
<td>1</td>
<td>210.5</td>
<td>3.2</td>
<td>7</td>
<td>1.50</td>
</tr>
<tr>
<td>1</td>
<td>Griffith</td>
<td>3</td>
<td>216.1</td>
<td>4.4</td>
<td>7</td>
<td>2.02</td>
</tr>
<tr>
<td>1</td>
<td>Griffith</td>
<td>5</td>
<td>212.5</td>
<td>4.1</td>
<td>7</td>
<td>1.95</td>
</tr>
<tr>
<td>1</td>
<td>Griffith</td>
<td>7</td>
<td>210.5</td>
<td>2.4</td>
<td>7</td>
<td>1.15</td>
</tr>
<tr>
<td>2</td>
<td>Griffith</td>
<td>9</td>
<td>210.3</td>
<td>1.0</td>
<td>7</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>Griffith</td>
<td>11</td>
<td>207.3</td>
<td>1.0</td>
<td>7</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>Griffith</td>
<td>13</td>
<td>201.3</td>
<td>0.9</td>
<td>7</td>
<td>0.43</td>
</tr>
<tr>
<td>2</td>
<td>Griffith</td>
<td>15</td>
<td>206.0</td>
<td>0.8</td>
<td>7</td>
<td>0.39</td>
</tr>
</tbody>
</table>
APPENDIX F. MODELLING CONTINUOUS EXPOSURE

F.1.1 Rounding Errors in Excel

To minimise errors, double precision arithmetic was used. A check on the errors in the calculations suggested by Nakamura (1991) revealed the following:

Table 35 Rounding errors

<table>
<thead>
<tr>
<th>Machine epsilon, $\varepsilon$</th>
<th>1.11E-16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rounding</td>
<td>-6.00E-11</td>
</tr>
</tbody>
</table>

The maximum possible rounding error is $\varepsilon/2$ or 0.5E-16 in any one calculation. The rounding error from adding 0.00001 to unity 10,000 times, was greater, but acceptable. Some of the solutions used 2,000 data sets, and integration using the trapezoidal method was used. This rounding error would account for much of the error.

F.1.2 Analytic Solution for Permeation Rate

The following is the listing for the Visual Basic for Applications code for the code "Flux". The function returned a value for a particular cell, using values in other cells (absolute, e.g. CPC thickness) or ranges of cells (relative, e.g. time). The function was then copied down a column to give a data set for plotting and analysis.
Listing 1 Permeation Rate Solution VBA code

Function Flux(Diffusion As Double, Solubility As Double, Thickness As Single, time As Single, Terms As Integer) As Double
' Using information in Goydan 1988 derived
' from Crank "Mathematics of Diffusion", Chapter 4
' also in Schwope 1988
' By David Bromwich, November 14 1997
' Diffusion: in cm2/s
' Solubility: in g/cm3
' Thickness: in cm
' Time: in seconds
' Terms: number of terms to sum over
On Error GoTo ErrorFlux
Dim j As Integer
Dim N As Integer
Dim sumflux As Double
Dim W As Double
Dim Pi As Double
Pi = 3.14159265358979 ' Had problems using PI()
W = Diffusion * time / (Thickness ^ 2) ' checks out
sumflux = 0
Dim Offset As Integer
Offset = 3
Dim term(5) As Double
Application.StatusBar = "Running Flux"

'sum terms
For j = 1 To Terms
    sumflux = sumflux + ((-1) ^ j) * Exp(-((Pi * j) ^ 2) * W)
Next j
Flux = (Diffusion * Solubility / Thickness) * (1 + 2 * sumflux)
'show other terms in offset cells
' ActiveCell.offset(0, 1).Range("A1").Value = Diffusion
' ActiveCell.offset(0, 2).Range("A1").Value = Time
' ActiveCell.offset(0, 3).Range("A1").Value = Thickness
' ActiveCell.offset(0, offset).Range("A1").Value = sumflux
' For j = 1 To 5
' offset = offset + 1
' ActiveCell.offset(0, offset + 1).Range("A1").Value = term(j)
' Next
Application.StatusBar = ""
Exit Function

ErrorFlux:
Application.StatusBar = ""
MsgBox ("Flux Error " + Err + Chr$(13) + Error$(Err))
Resume
End Function

The nominal data used by Schwope (and adopted as the part of the Standard Conditions, given in Chapter 6) to calculate curves were -

- Thickness of sample 0.05 cm (50 μm)
- Diffusion coefficient 2.5 E-6 cm² min⁻¹
- Solubility 4.9 E4 μg cm⁻³
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F.1.3 Analytic Performance of Permeation Rate Solution

To apply the solution to experimental data, the analytic limitations of the solution had to be investigated. The more terms in the solution, the closer the calculation would be to the exact solution. Sufficient accuracy had to be obtained within a few seconds for a large number of data points to make the solution practicable. This was particularly important for BT, as this occurred at low times when the inaccuracies in the solution could be expected to be greatest.

The number of terms required to give a curve that could be used to estimate Breakthrough Time was of interest, as divergence of a solution from measured values needed to be understood.

Zero to five term permeation rate solution

The permeation rate was calculated from 0.01 minutes to 100,000 minutes using zero to five terms in the equation. The data shows trailing zeros, indicating truncation or rounding of the calculations.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>0.1</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>1</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>2</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>3</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>5</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>10</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>20</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>30</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>100</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>300</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>1000</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>3000</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
<tr>
<td>10000</td>
<td>2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000 2.44999996349121600000</td>
</tr>
</tbody>
</table>

These values are plotted in Figure 215, and show the permeation curves converging as time increases and the poor performance of the Permeation Rate Solution when time and the number of terms are small. Clearly, for CPC permeation, a small number of terms is inadequate for modelling BT's less than 100 minutes.
When the series expansion of the diffusion equation is calculated with an even numbers of terms the permeation rate is positive, but the curve is not the familiar sigmoidal shape when the time is very small. The zero-term curve is the steady state permeation rate. For times greater than 100 minutes, the curves converge. It is evident that better precision is needed to estimate BT’s of 0.1 \( \mu \)g cm\(^{-2}\) min\(^{-1}\) required for nBT measurements.

**Effect of number of terms in permeation rate calculations**

To view the convergence of the permeation rate curves with an increasing number of terms, the solutions using an even numbers of terms are presented, to make the convergence easier to follow.
A sigmoidal permeation curve is increasingly evident with an increasing number of terms.

The asymptote approximated by the 100-term curve is the near-zero permeation predicted by the solution. Gains were made in the convergence of the series up to 100 terms for the first five minutes. Below 5 minutes, there were still errors, limited by the computational precision of the software, with small negative values returned at 1 and 3 minutes, even with 1000 terms. "Breakthrough" in most reasonable selections of CPC – chemical combinations occurs within tens of minutes, indicating that the Permeation Rate solution, as used with a spreadsheet, is probably sufficient for practicable purposes. Its general applicability could be tested over a range of thicknesses, diffusion coefficients and solubilities.

As there were no practical gains in 1000 terms over 100, it was decided to use 100 terms routinely in all calculations.

**F.1.4 Cumulative Permeation Solution**

The series expansion equation for Cumulative Permeation was readily coded in Visual Basic for Applications (VBA) for use within Excel.
When the initial matrix concentration and inside surface concentrations are zero, the Cumulative Permeation equation reduces to

\[ Q_t = \frac{DC_1 t}{l} - \frac{1}{6} \sum_{n=1}^{\infty} \frac{C_1 \cos(n\pi)}{n^2} \left( \frac{1 + e^{-D\frac{t}{l}n^2\pi}}{t} \right) \]

......Equation 31 Cumulative permeation solution

When \( t \) is large, the asymptotic expression for \( Q_t \) is

\[ Q_t = \frac{DC_1 t}{l} \left( 1 - \frac{l^2}{6D} \right) \]

... Equation 32 Cumulative permeation asymptote

This has the intercept \( \theta \) on the time axis of

\[ \theta = \frac{l^2}{6D} \]

...........................................Equation 33 Lag Time

This intercept is called the Lag Time and directly gives the Diffusion Coefficient, \( D \).

The slope of the line is also known as the Permeability \( P \) and is the Steady State Permeation Rate

\[ P = \frac{DC_1}{l} \]

...........................................Equation 34 Permeability

If the Diffusion Coefficient derived from the Lag Time is substituted in the expression for the Permeability, the surface concentration may be calculated. This concentration also the Solubility, \( S \) of the chemical in the CPC.

The equation can also be written as

\[ P = D.S \]

...........................................Equation 35 Permeability

where \( S = \frac{C_1}{l} \) is the Solubility.

The equation has been translated to VBA for use within Excel and the code is shown below. The equation allows for initial uniform concentrations in the membrane and a non-zero concentration on the inside of the CPC. A generalised version of the code is shown in Listing 2.
Listing 2 Cumulative Permeation Solution in VBA Code

```vba
Function Crank424(N As Integer, _
C0 As Double, C1 As Double, C2 As Double, _
D As Double, T As Double, L As Double) As Double
' see Crank "The Mathematics of Diffusion"
' page 51 equation 4.24 (c.f. 4.24a, a simplified version of 4.24)
' allows for different conc on each side
' January 8 1998
'
' N is number of terms
' C0 is initial uniform concentration in the membrane matrix (ug.cm3)
' C1 is initial concentration on surface of membrane (same as solubility, ug/cm3)
' C2 is the concentration on the inside surface of the membrane (ug/cm3)
' D is Diffusion coefficient (cm2/min)
' T is Time (minutes)
' L is Thickness (cm)
' V is the volume for closed loop permeation
' W = DT/L2
Dim Sum1, Sum2, W As Double
Dim j As Integer
Dim Pi, Pi2 As Double
Pi = 3.14159265358979
Pi2 = Pi ^ 2
Sum1 = 0
Sum2 = 0
W = D * T / L ^ 2
For j = 1 To N
    Sum1 = Sum1 + (C1 * Cos(j * Pi) - C2) / j ^ 2 * (1 - Exp(-W * (j * Pi) ^ 2))
Next j
If C0 > 0 Then 'speeds calculation if C0 is zero
    For j = 1 To N
        Sum2 = Sum2 + (1 / (2 * j - 1) ^ 2) * (1 - Exp(-W * ((2 * j - 1) * Pi) ^ 2))
    Next j
End If
Crank424 = W * L * (C1 - C2) + 2 * L / Pi2 * Sum1 + 4 * C0 * L / Pi2 * Sum2
End Function
```

With poor collecting flow patterns, the concentration of challenge chemical would be non zero on the inside surface of a CPC sample in a permeation cell. With the closed loop system, the effect would be more pronounced where there is poor mixing of the permeant with the collecting fluid.

**Effect of number of terms in cumulative permeation calculations**

As for the calculation of Permeation Rate, trials were performed to investigate the effect of number of terms on Cumulative Permeation. This is shown in Figure 217 on both linear and log-log scales.

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The differences are highlighted in the lower graph in Figure 217 by using log-log scales, as most of the errors occurred at low cumulative permeation values at small times. Adequate precision was obtained with 100 terms.

**F.1.5 Diffusivity and Solubility Re-calculation**

A solution allows the input conditions to be known exactly. Using the function "Crank424()", permeation curves were calculated with and without the chemical building up in the collecting medium for open loop and closed loop permeation,
respectively. Any simple non-continuous solution will tend to underestimate the effect of build-up, as estimates of the build-up will always lag the solution by the interval between the calculations. In the case of zero build-up, (which may be effectively achieved in open loop testing) this is not a concern. A check of the utility of the solution for low times was obtained by re-calculating the initial parameters.

**F.1.6 Closed Loop Cumulative Permeation**

![Figure 218 Closed Loop permeation, very large times](image)

The Cumulative Permeation solution clearly fails at very large times, as the permeation must reverse to decrease. This is thermodynamically impossible. The degree of departure increases with time, as shown from the departure from the straight line representing the zero concentration build-up. Two time intervals were chosen for evaluation – between 480 and 1,000 minutes – long times (shown in Figure 219) but not unrealistic, and 10,000 and 30,000 minutes (near the beginning of Figure 218).
The Lag Times were calculated from the intercept of the line for these intervals. From this the Diffusion Coefficient "D" was calculated and then this was then used to calculate the Solubility per unit thickness \( (S = \frac{C}{l}) \) from the slope of the intercept line. The errors in "D" and "\( S/l \)" were then calculated.

**Table 37 Closed loop, re-calculation of D and S/l from data**

<table>
<thead>
<tr>
<th></th>
<th>Open Loop</th>
<th>Closed Loop</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>480 to 1000 minutes</strong></td>
<td></td>
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<tr>
<td>Slope</td>
<td>2.442</td>
<td>2.440</td>
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<td>LT</td>
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<td>163.69</td>
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<td>D</td>
<td>2.54E-06</td>
<td>2.55E-06</td>
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<td>error D %</td>
<td>-1.74</td>
<td>-1.82</td>
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<tr>
<td>S/l</td>
<td>4.80E+04</td>
<td>4.79E+04</td>
</tr>
<tr>
<td>error S/l %</td>
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<td>2.20</td>
</tr>
<tr>
<td><strong>10000 to 30000 minutes</strong></td>
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<td></td>
</tr>
<tr>
<td>Slope</td>
<td>2.450</td>
<td>0.980</td>
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<tr>
<td>LT</td>
<td>166.67</td>
<td>16.98</td>
</tr>
<tr>
<td>D</td>
<td>2.50E-06</td>
<td>2.45E-05</td>
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<tr>
<td>Error D %</td>
<td>0.00</td>
<td>-881.56</td>
</tr>
<tr>
<td>S/l</td>
<td>4.90E+04</td>
<td>2.00E+03</td>
</tr>
<tr>
<td>Error S/l %</td>
<td>0.00</td>
<td>95.93</td>
</tr>
</tbody>
</table>

For Open Loop permeation in the collecting medium, the errors in "D" and "\( S/l \)" were close to 2%, but vanished at the larger times, as the slope became its asymptotic value. The reverse occurred with Closed Loop permeation, with similar size errors increasing to unacceptable levels as the concentration gradient fell and the concentration in the collecting medium changed to 1.5% of the solubility per unit thickness in the CPC.
medium. Schwope (1988) suggests that a figure of 20% on the solubility in the collecting medium is acceptable.
APPENDIX G. NUMERIC MODELLING OF INTERMITTENT EXPOSURES

The implementation of the Simple numeric solution and Explicit numeric solution are presented in this Appendix, as the Implicit numeric solution is described in Chapter 11. Both solutions were implemented using an Excel'97 spreadsheet. Figure 133 from Chapter 11 is reproduced below as Figure 130 with the three approaches.

Details of the validation of the Implicit solution and the code for calculating random intermittent exposures are also given.

SECTION G.1 SIMPLE NUMERIC SOLUTION

The membrane was initially "divided" into 100 layers and values for successive times obtained by averaging the values in neighbouring layers. The time interval, \( \tau \) between measurements was derived (Crank, 1975) as

\[
\tau = \frac{\ell^2}{2N^2D}
\]

......................... Equation 36 Time interval \( \tau \)

where

- \( \ell \) is the sample thickness (0.05 cm, 50 \( \mu m \))
- \( N \) is number of slices of CPC (nominally 10)
- \( D \) is the diffusion coefficient (2.5E-6 cm\(^2\) min\(^{-1}\))

A matrix based on averaging of successive layers as indicated in Figure 130 was constructed. The boundary conditions emulated intermittent exposure and zero concentration on the collecting surface were calculated along the time axis. For intermittent exposure for a membrane thickness \( L \) and initially dry they were

Initial, \( t = 0 \), \( C(0, 0) = 0, C(L, 0) = 0 \)

Time \( T \), \( t = T \) \( C(0, T) = C(t), \ C(L, t) = 0 \)

where \( C(t) = C \) for \( t = t \mod \) cycle time to \( t + \) wet time
It was found that if the number of layers was decreased from 100 to 10, the emerging oscillatory permeation rate pattern strengthened due to the reduced effect of successive averaging between layers. The Simple solution also had the instabilities mentioned by Crank (1975). The solution was initially implemented for continuous exposure and then the boundary conditions were changed to simulate intermittent exposure.

**G.1.1 Simple Solution, Continuous Exposure**

Standard Conditions were used (Chapter 6), except that the initial concentration was set at 1,000,000 to give larger numbers. The solution oscillated badly on alternate values. The experiment duration was 117 minutes with values calculated for 3 second intervals. The oscillations were eliminated by averaging adjoining values and the continuous permeation rate solution is shown in Figure 221.

\[
= 0 \text{ otherwise}
\]

There was a decrease after 100 minutes. This is an artefact of the discrete nature of the solution.

**G.1.2 Intermittent Exposure using Simple Numerical Solution**

For intermittent exposure, the boundary conditions on the "outside" of the CPC were modified. This was done with a conditional Excel formula

\[
IF(MOD(INT(time), interval=0, wet conc, dry conc)
\]

Figure 221 Simple numeric solution with 100 layers, smoothed

There was a decrease after 100 minutes. This is an artefact of the discrete nature of the solution.
used for the column labelled "Outside" in Table 38. The time interval \( \tau \) between measurements, was determined by Equation 36. The wet time and cycle time could also be set. Some of the data at 30 second "intervals" for 10 layers and a diffusion coefficient of 2.5E-5 cm²min⁻¹ (rather than \( D = 2.5E-6 \) cm²min⁻¹ with Standard Conditions) are shown in Table 38. The permeation rate used here is the concentration in the last layer, but could be corrected by the diffusion coefficient and the layer thickness to give the true permeation rate.

### Table 38 Simple numeric solution, intermittent exposure

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<th>Time (s)</th>
<th>Outside Conc.</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L4</th>
<th>L5</th>
<th>L6</th>
<th>L7</th>
<th>L8</th>
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<th>PR</th>
<th>Inside Conc.</th>
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</table>

Here, the concentration values propagate in pairs, corresponding to the pair of input values for the Simple solution.
Appendix G Numeric Modelling of Intermittent Exposures

G.1.3 Simple Intermittent Solution, Effect of Diffusion Coefficient

Two calculations were made of intermittent permeation for slightly different diffusion coefficients (2.5E-5 to 2.0E-5 cm²/min⁻¹), with a 15-minute cycle starting with one minute of chemical exposure. These data are plotted in Figure 222.

![Figure 222 Simple solution, 15 minute exposure intervals, varying D](image)

The chemical with the larger diffusion coefficient (2.5E-5 cm²/min⁻¹) permeated more quickly and approached a steady state pattern faster. However, with intermittent exposure, the permeation out of the CPC was also quicker, so that the chemical with the smaller diffusion coefficient (2.0E-5 cm²/min⁻¹) paradoxically attains a higher average permeation rate, if the solubilities are the same. This is yet to be demonstrated in practice, and adjustments for solubility differences between chemicals would have to be made to allow comparisons to be made.

The rate of propagation of a change through the layers was also limited by the "measurement" interval, as seen by the different BT for the two curves. The "outside" concentration puts a cap on its magnitude, but the diffusion coefficient also had an effect. The shape of the curves are similar to the experimental curves published in the ASTM F1383-1996 standard for intermittent exposure of CPC.

A disadvantage of the Simple solution was that oscillations were easy to produce, which limited its versatility. The stepped appearance is due to the pairs of high "outside" levels propagating together and the discrete times in the solution.
SECTION G.2  EXPPLICIT FINITE-DIFFERENCE NUMERIC SOLUTION

G.2.1  Explicit Numeric Solution Theory

The concentration $c$ in layer "i" at time "j" can be estimated using the concentrations in the adjoining layers "i+1" and "i-1" at time "j-1".

If $C = cC_0$ then Fick's Second law becomes

$$\frac{\partial c}{\partial T} = \frac{\partial^2 c}{\partial X^2}$$

.......................  Equation 37  Fick's Second Law

A Taylor's series expansion in the T direction with X constant is

$$c_{i,j+1} = c_{i,j} + \delta T \left( \frac{\partial c}{\partial T} \right)_{i,j} + \frac{1}{2} (\delta T)^2 \left( \frac{\partial^2 c}{\partial T^2} \right)_{i,j} + ..., $$

.......................  Equation 38  Concentration in layer

where

- $c_{i,j+1}$ is the concentration in the $i^{th}$ layer at time $j+1$
- $c_{i,j}$ is the concentration in the $i^{th}$ layer at time $j$
- $\delta T$ is the time increment

Re-arranging gives

$$\left( \frac{\partial c}{\partial T} \right)_{i,j} = \frac{c_{i,j-1} - c_{i,j+1}}{\delta T} + O(\delta T)$$

.......................  Equation 39  Fick's Second Law

where $O(\delta T)$ is an error term

Similarly for the X direction, keeping T constant for the adjoining layers

$$c_{i+1,j} = c_{i,j} + \delta X \left( \frac{\partial c}{\partial X} \right)_{i,j} + \frac{1}{2} (\delta X)^2 \left( \frac{\partial^2 c}{\partial X^2} \right)_{i,j} + ..., $$

.......................  Equation 40  Concentration in layer

$$c_{i-1,j} = c_{i,j} - \delta X \left( \frac{\partial c}{\partial X} \right)_{i,j} + \frac{1}{2} (\delta X)^2 \left( \frac{\partial^2 c}{\partial X^2} \right)_{i,j} + ..., $$

.......................  Equation 41  Concentration in layer

Adding these terms gives
\[ \left( \frac{\partial^2 c}{\partial X^2} \right)_{i,j} = \frac{c_{i+1,j} - 2c_{i,j} + c_{i-1,j}}{(\delta X)^2} + O(\delta X)^2 \]

........................................... Equation 42 Fick's Second Law

where \( O(\delta X)^2 \) is the error term.

Substituting these two forms in Fick's Second Law, as modified gives

\[ c_{i,j+1} = c_{i,j} + r \left( c_{i,j} - 2c_{i,j} + c_{i+1,j} \right) \]

........................................... Equation 43 Concentration in layer

where \( r = \frac{\delta T}{(\delta X)^2} \)

When \( r = \frac{1}{2} \) the Explicit solution is the same as the Simple solution, but more stable and less likely to oscillate.

### G.2.2 Formulating the Explicit Solution for a Spreadsheet

The Explicit solution was coded to allow measured values of the diffusion coefficient to be used and the initial condition to be set so that exposure occurred for one minute of an exposure drying cycle. The time interval between calculations "\( \tau \)" was calculated as

\[ \tau = r \left( \frac{CPC_{\text{thickness}}}{slices} \right)^2 \]

........................................... Equation 44 Time interval \( \tau \)

Figure 223 shows the implementation of the solution using Microsoft Excel'97. The CPC has been divided into 10 slices "L1" to "L9" and "Dry". The concentration on the exposed side was nominally 10,000, to give easy numbers on the graph. A similar formula,

\[ =\text{IF(MOD(INT(time*100), cycletime*100), wet period * 100)} \leq 0, \text{wet conc, dry conc)} \]

......... Equation 45 Modulo formula for cycle time

was applied to calculate the wet concentration at a given time. The factor of 100 allowed the cycle time and wet time to be changed in increments of 1/100. This formula was used in the column "outside" to automatically give an exposure of a predetermined duration at the beginning of each Wet Period. Figure 223 shows the propagation of the calculations for the first 10 minute Wet Period, and the beginning of the rest of the cycle which is "dry".
Appendix G Numeric Modelling of Intermittent Exposures

Figure 223 Explicit solution, showing propagation of permeation

Initial values at "A" propagate to the right, changed by the values in the three cells above the cell being calculated, as shown by the arrows. The gradient between Layer L9 "B" and DRY is scaled with the thickness of the layer "dX" and the diffusion coefficient to give the permeation rate "C" in $\mu g \, cm^{-2} \, min^{-1}$. The label "D" better shows the influence of a cell in both directions.

**Operation of the Explicit solution**

For convenience, the graphical representation of the Explicit solution was embedded in the spreadsheet, as shown in Figure 224. This permitted the shape of the plot to be immediately observed. The spreadsheet tag was automatically named using the solution parameters, and a GIF file of the plot saved using these parameters in the file name for easy identification.
The solution parameters are arranged along the top of the figure. The columns "L1" to "L9" plus "DRY" (4th row) calculated the concentrations through the thickness of the CPC at thickness intervals "dX". The four columns on the right are the calculated permeation rate, the trapezoidal integral of this rate (cumulative permeation), the analytic permeation rate and analytic cumulative permeation. The Explicit solution, with 2000 time increments and 100 terms for each point in the analytic solution took ten seconds to evaluate on a PC (Dell, Intel Pentium 133 processor).

**Instabilities from implementation of Explicit solution**

The Explicit solution had instabilities relating to its implementation, but these tended to be moderate for \( r << 0.5 \). One such instability is shown in Figure 225.
At first, it was thought that this instability was inherent in the Explicit solution, but the behaviour was traced to certain values of $r$ that created cyclic excursions due to the method of calculating wet times. This had allowed an occasional extra calculation of wet time to creep in, effectively increasing the total wet time and creating the cyclic excursions from the periodic pattern. These drifts become more apparent when $r$ approached 0.5, as the number of calculations for each cycle decreased.

SECTION G.3  VALIDATION OF CRANK- NICOLSON IMPLICIT SOLUTION

Though several texts indicated the method is widely used, there was a need to check the code when used with a spreadsheet. An example using the solution is given by Crank (1975, page 145, with tabulated results in Table 8.3). The example is a special condition of the solution presented, in that for $r = 1$, one term is zero on the right hand side of the equation. The example had 10 layers such that the concentration $c$ was

$$ c = 2X, \quad 0 \leq X \leq \frac{1}{2}, \quad T = 0 $$

$$ c = 2(1-X), \quad \frac{1}{2} \leq X \leq L, \quad T = 0 $$

with zero boundary conditions maintained. Crank outlines a solution utilising the symmetry of the concentration profile, but for modelling the permeation of CPC, such symmetry would rarely exist, and the full calculation of the concentration profile at different times was required.
For \( r = 1 \), the coefficients in left hand side of the equation is represented by matrix A

<table>
<thead>
<tr>
<th>Table 39 Matrix A (9x9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4         -1         0         0         0         0         0         0         0         0</td>
</tr>
<tr>
<td>-1        4         -1         0         0         0         0         0         0         0</td>
</tr>
<tr>
<td>0         -1        4         -1         0         0         0         0         0         0</td>
</tr>
<tr>
<td>0         0         -1        4         -1         0         0         0         0         0</td>
</tr>
<tr>
<td>0         0         0         -1        4         -1         0         0         0         0</td>
</tr>
<tr>
<td>0         0         0         0         -1        4         -1         0         0         0</td>
</tr>
<tr>
<td>0         0         0         0         0         -1        4         -1         0         0</td>
</tr>
<tr>
<td>0         0         0         0         0         0         -1        4         -1         0</td>
</tr>
<tr>
<td>0         0         0         0         0         0         0         -1        4         0</td>
</tr>
</tbody>
</table>

The coefficients in the right hand side by the matrix "B"

<table>
<thead>
<tr>
<th>Table 40 Matrix B (11x9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1         0         0         0         0         0         0         0         0         0         0</td>
</tr>
<tr>
<td>0         1         0         0         0         0         0         0         0         0         0</td>
</tr>
<tr>
<td>1         0         1         0         0         0         0         0         0         0         0</td>
</tr>
<tr>
<td>0         1         0         1         0         0         0         0         0         0         0</td>
</tr>
<tr>
<td>0         0         1         0         1         0         0         0         0         0         0</td>
</tr>
<tr>
<td>0         0         0         1         0         1         0         0         0         0         0</td>
</tr>
<tr>
<td>0         0         0         0         1         0         1         0         0         0         0</td>
</tr>
<tr>
<td>0         0         0         0         0         0         1         0         1         0         0</td>
</tr>
<tr>
<td>0         0         0         0         0         1         0         1         0         0         0</td>
</tr>
<tr>
<td>0         0         0         0         0         0         0         1         0         0         0</td>
</tr>
</tbody>
</table>

Multiplying the inverse of Matrix A by Matrix C gave Matrix CA\(^{-1}\). The numbers have been rounded to four decimal places for tabulation.

<table>
<thead>
<tr>
<th>Table 41 Matrix CA(^{-1}) (11x9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2679   0.0718   0.0192   0.0052   0.0014   0.0004   0.0001   0.0000   0.0000   0.0000</td>
</tr>
<tr>
<td>0.0718   0.2872   0.0770   0.0206   0.0055   0.0015   0.0004   0.0001   0.0000   0.0000</td>
</tr>
<tr>
<td>0.2872   0.1487   0.3078   0.0825   0.0221   0.0059   0.0016   0.0004   0.0001   0.0001</td>
</tr>
<tr>
<td>0.0770   0.3078   0.1543   0.3093   0.0829   0.0222   0.0059   0.0016   0.0004   0.0004</td>
</tr>
<tr>
<td>0.0206   0.0825   0.3093   0.1547   0.3094   0.0829   0.0222   0.0059   0.0016   0.0001</td>
</tr>
<tr>
<td>0.0055   0.0221   0.0829   0.3094   0.1547   0.3094   0.0829   0.0221   0.0055   0.0055</td>
</tr>
<tr>
<td>0.0015   0.0059   0.0222   0.0829   0.3094   0.1547   0.3094   0.1543   0.0825   0.0206</td>
</tr>
<tr>
<td>0.0004   0.0016   0.0059   0.0222   0.0829   0.3093   0.1543   0.3078   0.0770   0.0770</td>
</tr>
<tr>
<td>0.0001   0.0004   0.0016   0.0059   0.0221   0.0825   0.3078   0.1487   0.2872   0.2872</td>
</tr>
<tr>
<td>0.0000   0.0001   0.0004   0.0015   0.0055   0.0206   0.0770   0.2872   0.0718   0.0718</td>
</tr>
<tr>
<td>0.0000   0.0000   0.0001   0.0004   0.0014   0.0052   0.0192   0.0718   0.2679   0.2679</td>
</tr>
</tbody>
</table>

Matrix CA\(^{-1}\) was then multiplied by the conditions in the previous period, including the boundary conditions, to get the new concentrations in the slices of the sample. This formula was then copied down the time line.
This example was used to check the construction of the solution. Table 42 shows the calculation of the solution rounded to four decimal places. Identical numbers were derived to those published by Crank (1975).

**Table 42 Crank-Nicolson Implicit solution validation**

<table>
<thead>
<tr>
<th>Time</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>0.010</td>
<td>0.1989</td>
<td>0.3965</td>
<td>0.5843</td>
<td>0.7738</td>
<td>0.9631</td>
<td>1.1534</td>
<td>0.9631</td>
<td>0.7738</td>
<td>0.5843</td>
<td>0.3965</td>
<td>0.1989</td>
</tr>
<tr>
<td>0.020</td>
<td>0.1936</td>
<td>0.3799</td>
<td>0.5397</td>
<td>0.6901</td>
<td>0.8406</td>
<td>1.0000</td>
<td>0.8406</td>
<td>0.6901</td>
<td>0.5397</td>
<td>0.3799</td>
<td>0.1936</td>
</tr>
<tr>
<td>0.030</td>
<td>0.1826</td>
<td>0.3515</td>
<td>0.4902</td>
<td>0.6215</td>
<td>0.7522</td>
<td>0.8834</td>
<td>0.7522</td>
<td>0.6215</td>
<td>0.4902</td>
<td>0.3515</td>
<td>0.1826</td>
</tr>
<tr>
<td>0.040</td>
<td>0.1683</td>
<td>0.3218</td>
<td>0.4461</td>
<td>0.5655</td>
<td>0.6826</td>
<td>0.8034</td>
<td>0.6826</td>
<td>0.5655</td>
<td>0.4461</td>
<td>0.3218</td>
<td>0.1683</td>
</tr>
<tr>
<td>0.050</td>
<td>0.1538</td>
<td>0.2932</td>
<td>0.4047</td>
<td>0.4770</td>
<td>0.5267</td>
<td>0.6461</td>
<td>0.5267</td>
<td>0.4770</td>
<td>0.4047</td>
<td>0.2932</td>
<td>0.1538</td>
</tr>
<tr>
<td>0.060</td>
<td>0.1399</td>
<td>0.2664</td>
<td>0.3672</td>
<td>0.4321</td>
<td>0.4569</td>
<td>0.5556</td>
<td>0.4569</td>
<td>0.3672</td>
<td>0.2664</td>
<td>0.1399</td>
<td>0.060</td>
</tr>
<tr>
<td>0.070</td>
<td>0.1270</td>
<td>0.2418</td>
<td>0.3330</td>
<td>0.3916</td>
<td>0.4119</td>
<td>0.4770</td>
<td>0.3916</td>
<td>0.3330</td>
<td>0.2418</td>
<td>0.1270</td>
<td>0.070</td>
</tr>
<tr>
<td>0.080</td>
<td>0.1153</td>
<td>0.2193</td>
<td>0.3019</td>
<td>0.3550</td>
<td>0.3733</td>
<td>0.3733</td>
<td>0.3550</td>
<td>0.3019</td>
<td>0.2193</td>
<td>0.1153</td>
<td>0.080</td>
</tr>
<tr>
<td>0.090</td>
<td>0.1045</td>
<td>0.1969</td>
<td>0.2738</td>
<td>0.2918</td>
<td>0.2918</td>
<td>0.2918</td>
<td>0.2738</td>
<td>0.1969</td>
<td>0.1045</td>
<td>0.090</td>
<td>0.090</td>
</tr>
<tr>
<td>0.100</td>
<td>0.0948</td>
<td>0.1803</td>
<td>0.2482</td>
<td>0.2918</td>
<td>0.3069</td>
<td>0.3069</td>
<td>0.2918</td>
<td>0.2482</td>
<td>0.1803</td>
<td>0.0948</td>
<td>0.100</td>
</tr>
</tbody>
</table>

| Analytic | 0.0934 | 0.1776 | 0.2444 | 0.2873 | 0.3021 | Average |
| % Diff   | -1.50  | -1.54  | -1.57  | -1.57  | -1.55  |

An analytic solution was also published by Crank (1975) and the analytic values are shown in bold in Table 42, along with calculations of the percentage difference for the highlighted numbers. The error in the solution was about -1.55%. There were no data to test the solution for \( r \neq 1 \), but small perturbations (0.01) from unity did not produce a large change in concentration, relative to the analytic error (Table 43), so gross errors could probably be discounted.

**Table 43 Effect of "r" on concentration**

<table>
<thead>
<tr>
<th></th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>0.0939</td>
<td>0.1786</td>
<td>0.2458</td>
<td>0.2890</td>
<td>0.3039</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0948</td>
<td>0.1803</td>
<td>0.2482</td>
<td>0.2918</td>
<td>0.3069</td>
</tr>
<tr>
<td>0.99</td>
<td>0.0957</td>
<td>0.1821</td>
<td>0.2507</td>
<td>0.2947</td>
<td>0.3099</td>
</tr>
</tbody>
</table>

**SECTION G.4 RANDOM INTERMITTENT EXPOSURES**

Though random intermittent exposures could be generated by the *GloveTest* system, it was possible to model such exposures. The code below was used for this simulation.

This code automatically generates a matrix of cells of time and "wet" values using values of measurement interval (DT or dT), Cycle Time (CT), wet time (WT), Experiment duration (Expt), Wet value (Wet) and Dry Value (Dry, normally zero). This approach could have been taken to generate the whole experiment. The choice of random or regular cyclic exposures was made using a "check box".
Listing 3 VBA code to calculate random wet cycles

```vba
Public Function Sum2() As Double
    ' Written 27 July 1998 by David Bromwich
    ' Sets up Times and Wet values for random exposures
    Worksheets(1).EnableCalculation = False
    Application.StatusBar = "calculating Wet Values and Times"
    Dim rwindex As Double, colindex As Double, DT As Double, CT As Double
    Dim Wt As Double, Expt As Double, Wet As Double, dry As Double, wetvalue As Double
    Dim LF As String
    LF = Chr$(13)
    'Set row for wet values and time
    rwindex = 35
    'Clear rows
    With ActiveSheet
        .Rows(rwindex).Clear
        .Rows(rwindex - 1).Clear
        .Rows(25).Clear
    End With
    'Grab Names from Sheet defined using Insert names
    ' - its easier to set values this way
    With ActiveWorkbook.Names
        DT = Range(.Item("dT"),.RefersTo) 'same names on sheet and here makes debugging easier
        CT = Range(.Item("CT"),.RefersTo)
        Wt = Range(.Item("WT"),.RefersTo)
        Expt = Range(.Item("Expt"),.RefersTo)
        Wet = Range(.Item("Wet"),.RefersTo)
        dry = Range(.Item("Dry"),.RefersTo)
    End With
    'Test that WT < CT
    If Wt > CT Then
        MsgBox "WT must be less than CT"
        Exit Sub
    End If
    'Label rows for time and wet
    Cells(rwindex - 1, 1).Value = "Time"
    Cells(rwindex, 1).Value = "Wet"
    Cells(rwindex - 1, 1).Font.Bold = True
    Cells(rwindex, 1).Font.Bold = True
    'Calculate number of columns from Experiment duration and time interval between calculations
    numcells = WorksheetFunction.RoundUp(Expt / DT, 1)
    For colindex = 2 To numcells + 1 'start from second column 'Calculate Wet values
        Application.StatusBar = "Calculating Wet Values and Times, Column " & colindex - 1
        ET = DT * (colindex - 2) 'Experiment time
        If ET <= Wt Then 'initial wet period at beginning
            wetvalue = Wet
            drynow = True
        Else
            If drynow = True Then ' run this once at the beginning of a dry cycle
                cyclelength = Rnd * CT * 2 ' use CT as average - means range can be twice
            Else
                cyclelength = CT
            End If
            DryTime = ET + cyclelength
            drynow = False
        End If
        If ET < DryTime Then
            wetvalue = dry
        End If
    Next colindex
End Function
Private Sub cmdRandom_Click()
    ' Written 27 July 1998 by David Bromwich
    ' Sets up Times and Wet values for random exposures
    Worksheets(1).EnableCalculation = False
    Application.StatusBar = "calculating Wet Values and Times"
    Dim rwindex As Double, colindex As Double, DT As Double, CT As Double
    Dim Wt As Double, Expt As Double, Wet As Double, dry As Double, wetvalue As Double
    Dim LF As String
    LF = Chr$(13)
    'Set row for wet values and time
    rwindex = 35
    'Clear rows
    With ActiveSheet
        .Rows(rwindex).Clear
        .Rows(rwindex - 1).Clear
        .Rows(25).Clear
    End With
    'Grab Names from Sheet defined using Insert names
    ' - its easier to set values this way
    With ActiveWorkbook.Names
        DT = Range(.Item("dT"),.RefersTo) 'same names on sheet and here makes debugging easier
        CT = Range(.Item("CT"),.RefersTo)
        Wt = Range(.Item("WT"),.RefersTo)
        Expt = Range(.Item("Expt"),.RefersTo)
        Wet = Range(.Item("Wet"),.RefersTo)
        dry = Range(.Item("Dry"),.RefersTo)
    End With
    'Test that WT < CT
    If Wt > CT Then
        MsgBox "WT must be less than CT"
        Exit Sub
    End If
    'Label rows for time and wet
    Cells(rwindex - 1, 1).Value = "Time"
    Cells(rwindex, 1).Value = "Wet"
    Cells(rwindex - 1, 1).Font.Bold = True
    Cells(rwindex, 1).Font.Bold = True
    'Calculate number of columns from Experiment duration and time interval between calculations
    numcells = WorksheetFunction.RoundUp(Expt / DT, 1)
    For colindex = 2 To numcells + 1 'start from second column 'Calculate Wet values
        Application.StatusBar = "Calculating Wet Values and Times, Column " & colindex - 1
        ET = DT * (colindex - 2) 'Experiment time
        If ET <= Wt Then 'initial wet period at beginning
            wetvalue = Wet
            drynow = True
        Else
            If drynow = True Then ' run this once at the beginning of a dry cycle
                cyclelength = Rnd * CT * 2 ' use CT as average - means range can be twice
            Else
                cyclelength = CT
            End If
            DryTime = ET + cyclelength
            drynow = False
        End If
        If ET < DryTime Then
            wetvalue = dry
        End If
    Next colindex
End Sub
```
Else
  wetvalue = Wet
  If ET >= (DryTime + Wt) Then drynow = True 'next cycle is dry
  End If
End If
Cells(rwindex - 1, colindex).Value = ET 'times
Cells(rwindex, colindex).Value = wetvalue
Cells(25, colindex).Value = wetvalue
'Cells(rwIndex + 1, colindex).Value = cyclelength 'Rnd * CT * 2
Next
Worksheets(1).EnableCalculation = Tr
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