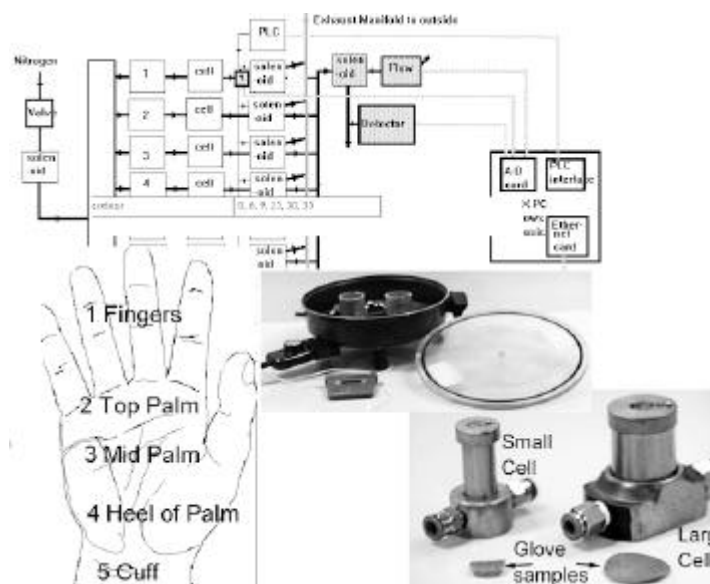


Worksafe Australia Research Project



“The Use of Gloves to Control Chemical Exposure in the Workplace”

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1. ABSTRACT

An automated eight-sample glove testing rig has been developed with *GloveTest* control and analysis software. A review of the literature and testing of gloves in the laboratory and field has revealed some little known and new aspects of glove performance in the workplace. There are also indications that the reasons for choice and wearing of chemical gloves are related more to cost and protection from smelly or dirty hands rather than chemical protection. A suite of performance indices has been developed and compared to explain variations in performance between gloves. Glove permeation as measured with a new biopsy test cell, the Griffith Small Cell, varies by about a factor of three over the surface of the PVC (Poly Vinyl Chloride) gloves commonly used in industry. This variation is much greater than the variation between new and used gloves or between gloves. Polymer science approaches have not been widely applied in understanding glove behaviour and testing and research should adopt knowledge from this field. Glove thickness can disproportionately affect the chemical diffusion through gloves by allowing temperature gradients. There is a need for glove manufacturers to publish the “three dimensional solubility parameter” for their gloves so that glove performance with mixtures may be estimated. There are major flaws in using existing standards, arising from the lack of statistical approaches to ranking gloves based on the testing protocols set out in the standards. The tests will only show real differences in glove performance when these are at least the same size as the index being measured. The new cells have been partially validated against the standard ASTM cell. Preliminary trials have been conducted with a novel intermittent cell to emulate intermittent workplace exposure which may be important if diffusion becomes strongly concentration dependent when the glove dries. Testing techniques such as FTIR and DSC used in polymer chemistry have been tried and show promise.. Work to further the understanding of the permeation process, including the effect of mixtures of solvents is continuing. Guidelines to complement existing selection and use rules have been developed and there are technical recommendations for manufacturers and for future research.

2. ACKNOWLEDGMENTS

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3. INDEX

1. ABSTRACT	1
2. ACKNOWLEDGMENTS	1
3. INDEX	2
3.1. <i>List of Figures</i>	4
3.2. <i>List of Tables</i>	5
4. GLOSSARY	6
5. INTRODUCTION	8
5.1. <i>Background</i>	8
5.2. <i>Work leading to this project</i>	8
6. AIMS	8
7. OBJECTIVES	9
8. LITERATURE REVIEW	9
8.1. <i>Sources of Information</i>	9
8.2. <i>Review of Literature</i>	10
8.3. <i>Guidelines for glove selection</i>	11
8.4. <i>Permeation Theory</i>	12
8.5. <i>Solubility Parameters</i>	13
8.6. <i>Polymer Science</i>	14
8.7. <i>Types of test cells</i>	15
8.8. <i>Flow rates and carrier gas</i>	17
8.9. <i>Detectors</i>	17
8.10. <i>Thickness of gloves</i>	17
8.11. <i>Duration of tests</i>	18
8.12. <i>Temperature and temperature control</i>	18
8.13. <i>Replications and statistical analysis</i>	18
8.14. <i>Skin</i>	19
8.15. <i>Mixtures of solvents and formulations</i>	19
8.16. <i>Decontamination of gloves</i>	19
8.17. <i>Weight gain and swelling</i>	20
8.18. <i>Use and re-exposure</i>	20
8.19. <i>Solids</i>	21
8.20. <i>Workplace Observations</i>	21
9. GloveTest DEVELOPMENT	22
9.1. <i>Initial approaches</i>	22
9.2. <i>GloveTest Hardware</i>	26
9.3. <i>Visual Basic and Programming</i>	33
9.4. <i>GloveTest Software</i>	34
10. GloveTest TRIALS	39
10.1. <i>Laboratory Trials</i>	39
10.2. <i>Calibration</i>	40
10.3. <i>Cell Validation</i>	43
10.4. <i>Pilot Trials</i>	45
10.5. <i>Main Trials</i>	46
10.6. <i>Intermittent Cell</i>	47
10.7. <i>Mixtures and Modelling</i>	48
10.8. <i>DSC</i>	48
11. RESULTS	49
11.1. <i>Laboratory Trials</i>	49
11.2. <i>Pilot Trials</i>	51
11.3. <i>Main Trials</i>	60

11.4.	<i>Qualitative</i>	76
11.5.	<i>Variation of Weight and Thickness</i>	77
11.6.	<i>Mixtures</i>	80
11.7.	<i>DSC Trials</i>	80
12.	DISCUSSION	82
12.1.	<i>Existing guidelines</i>	82
12.2.	<i>New vs Used</i>	82
12.3.	<i>Front-Back</i>	82
12.4.	<i>Fingers to Cuff</i>	82
12.5.	<i>Use and Position</i>	83
12.6.	<i>Solvent</i>	83
12.7.	<i>Mixtures</i>	83
12.8.	<i>Australian vs Imported</i>	83
12.9.	<i>Relevance of Test Results</i>	84
12.10.	<i>Validation and calibrations</i>	84
12.11.	<i>Were Aims and Objectives met?</i>	84
13.	RECOMMENDATIONS	86
13.1.	<i>User Recommendations</i>	86
13.2.	<i>Technical Recommendations</i>	86
13.3.	<i>Research Recommendations</i>	86
14.	BIBLIOGRAPHY	87
15.	APPENDICES	90
15.1.	<i>Appendix A: Initial Report to Worksafe</i>	90
15.2.	<i>Appendix B: Reports for Safework</i>	90
15.3.	<i>Appendix C: Ethics and Workplace Agreement</i>	90
15.4.	<i>Appendix D: Hardware</i>	95
15.5.	<i>Appendix E: National Safety Council Guidelines</i>	96
15.6.	<i>Appendix F: Laboratory Trials Data</i>	98
15.7.	<i>Appendix G: Pilot Trials Data</i>	99
15.8.	<i>Appendix H: Main Trials Data</i>	104
15.9.	<i>Appendix I: Glove Papers by Investigators</i>	108
15.10.	<i>Appendix J: FTIR Output</i>	109
15.11.	<i>Appendix K: Statistical Tools</i>	110
15.12.	<i>Appendix L: Software Disk - GloveTest program and Data</i>	111

3.1. List of Figures

Figure 1 Nominal Test Rig Schematic	23
Figure 2 Actual Test Rig Schematic (Simplified)	24
Figure 3 Test rig on mounting board	24
Figure 4 HNU photo-ionisation detector	25
Figure 5 Eight Channel PLC	29
Figure 6 Cell Clamp for clamping Cells	29
Figure 7 Festo Solenoid	30
Figure 8 A-D Card (16 channel 12 bit)	31
Figure 9 486SX personal computer	32
Figure 10 Mass Flow Transducer	32
Figure 11 Temperature transducer	32
Figure 12 Vacuum oven	33
Figure 13 GloveTest Menu	36
Figure 14 Screen for Analysis Module	37
Figure 15 GloveTest Program Modules	37
Figure 16 Photoionisation detector calibration	41
Figure 17 ASTM Cell	41
Figure 18 Griffith Large Cell	42
Figure 19 Griffith Small Cell	42
Figure 20 Validation of Griffith Cells	43
Figure 21 Mixing Chambers	43
Figure 22 Gas supply and solenoid problems	44
Figure 23 Run F-2 Cell Validation	45
Figure 24 Measuring glove thickness	46
Figure 25 Intermittent Cell	47
Figure 26 Variation in BT with gloves with Position	55
Figure 27 Variation in BT between Ansell PVC gloves	56
Figure 28 Variation in LT between Ansell PVC gloves	57
Figure 29 Variation in SSPR between Ansell PVC gloves	57
Figure 30 New Ansell PVC gloves: BT and Position	58
Figure 31 Used Ansell PVC gloves, BT and Position	58
Figure 32 Used and New Ansell PVC gloves, BT compared by position	59
Figure 33 SSPR: New MSA Metalguard gloves	62
Figure 34 SSPR: Used MSA Solvanguard gloves	62
Figure 35 SSPR: New Double Dipped PVC gloves	63
Figure 36 Used MSA Solvanguard gloves	64
Figure 37 BT - New and Used Ansell PVC gloves	71
Figure 38 New and Used BT, matched for position	72
Figure 39 LT - New and Used Ansell PVC gloves	73
Figure 40 New and Used LT, matched for position	73
Figure 41 SSPR - New and Used Ansell PVC gloves	74
Figure 42 New and Used SSPR, matched for Position	75
Figure 43 New and Used Integral Permeations	76
Figure 44 Large Cell: Variation of sample Thickness and Weight	79
Figure 45 Small Cell: Variation of sample Thickness and Weight	79

3.2. List of Tables

Table 1 Comparison of this project with Jencen (1989)	10
Table 2 Effect of glove material on permeation	10
Table 3 Application of thin film theory to gloves	10
Table 4 Effect of solubility on models	14
Table 5 Modifications to ASTM cell	16
Table 6 Effect of glove thickness on damage	18
Table 7 4H glove guide - mixtures	19
Table 8 Repeated Thermal Decontamination (Menke 1988)	20
Table 9 Re-use of Gloves (after Fosberg 1988)	21
Table 10 Changes to Rig Design	26
Table 11 GloveTest Hardware	27
Table 12 Cell comparisons	28
Table 13 A-D Specifications	31
Table 14 GloveTest Program Global Variables	35
Table 15 Detector Characteristics	40
Table 16 Number of measurements to detect real differences between glove selections	50
Table 17 Detectable percentage difference for sample size	51
Table 18 Codes for Glove Sample Position	51
Table 19 Codes for Glove Type	52
Table 20 Chemicals used at Pilot Trials site	54
Table 21 Variation with position of indices between gloves	56
Table 22 Number of Measurements	60
Table 23 Industries participating in project	61
Table 24 Codes for correlation tables	65
Table 25 Codes for Glove Position and Glove Type	65
Table 26 Probabilities SSPR are different - back of a new double dipped PVC glove	66
Table 27 Selected Correlation Probabilities	67
Table 28 Effect of Position and Use: Ansell PVC gloves	70
Table 29 Integral Permeation: New and Used Ansell PVC gloves by Position	75
Table 30 Comments on glove use	77
Table 31 Sartorius M5 Balance calibration	78
Table 32 Variation of Thickness and Weight of samples from same part of PVC glove	78
Table 33 Mixtures for FTIR Trials	80
Table 34 Effect of Glove Type, Position and Use on Performance Indices	83
Table 35 Suppliers of Parts	95
Table 36 Codes for Glove Position and Glove Type	99
Table 37 New Ansell double dipped PVC (type 2B)	100
Table 38 Confidence Intervals - New Ansell PVC double dipped gloves	101
Table 39 New Ansell PVC gloves - Effect of position on five indices	102
Table 40 Used Ansell PVC gloves - Effect of position on five indices	103
Table 41 Codes for table columns	104
Table 42 Section of Correlation Table	104
Table 43 Correlation Table	105

4. GLOSSARY

4.1.1. Arrhenius

Permeation follows an Arrhenius type relationship when it follows a negative exponential relationship with temperature.

4.1.2. MSDS

Material Safety Data Sheet. An information sheet on the safe use, storage and disposal of a chemical or formulation.

4.1.3. CPC

Chemical Protective Clothing. Usually gloves, but it can include chemical suits, aprons and boots.

4.1.4. Fickian diffusion

Simple Fickian diffusion is said to occur when the rate of diffusion depends only on the concentration gradient and a constant diffusion coefficient.

4.1.5. AS

Australian Standard. A standard published by Standards Australia and often adopted by legislation or by manufacturers.

4.1.6. ASTM

American Society for Testing and Measurement. The American equivalent of Standards Australia. The reference cell in this project is specified by ASTM F739 1985

4.1.7. BT

Breakthrough Time. The time of first discernible permeation of a glove by a chemical. This is variously defined in terms of detection limits (often 3 standard deviations of the background noise signal of the detector) or more easily in terms of the time intercept of the open loop permeation curve. If expressed in terms of detection limits, different manufacturers will give very different results, with gloves from the least sensitive detector appearing to be best.

4.1.8. DOS

Disc Operating System. The program loaded into a computer when it is turned on to enable information to be transferred to and from a disk drive. On PC's it normally is stored on an internal hard disk drive and also allows a complex setup and operation of the computer. In the project Microsoft DOS version 6.1 was used.

4.1.9. DSC

Differential Scanning Colorimetry. A standard technique in polymer chemistry for determining structural changes in polymers. The specific heat of the polymer changes as it is heated, and invisible structural changes will be revealed.

4.1.10. FTIR

Fourier Transform Infra Red. A relatively new form of infra red analyser which performs a Fast Fourier Transform on the signal from an infra red beam measuring the amount of light absorbed by a sample and giving a near instant spectrum. For this experiment, the rapid calculation of the IR absorption spectrum allows successive IR spectra to be made whilst a mixture of solvents is permeating a glove. The relative rates of permeation of each solvent may then be estimated.

4.1.11. INT20

Integral 20 minutes. The amount of solvent passing through a sample of a glove in a test cell in the first twenty minutes

4.1.12. INT30

Integral 30 minutes. The same as INT20 but for 30 minutes.

4.1.13. ISO

International Standards Organisation. The International Equivalent of Standards Australia. The ISO cell is similar to the much simpler Griffith Cell used in this project.

4.1.14. LT

Lag Time. The time intercept of the closed loop permeation curve or (almost identically) the time intercept of the integral of the open loop permeation curve. LT is less experiment dependent parameter than BT.

4.1.15. PC

Personal Computer. A desktop computer. In this project, a generic 486SX was used.

4.1.16. PLC

Programmable Logic Controller. A device for controlling machines, with built in computer programmed logic. In this experiment, a PLC card and PC were used to become a very flexible PLC.

4.1.17. PVC

Poly Vinyl Chloride. A common polymer used in gloves. Usually a blend of PVC, plasticisers and fillers.

4.1.18. SSPR

Steady State Permeation Rate. The relatively fixed rate with which chemicals penetrate gloves after an initial settling-in period. Usually expressed in weight of solvent per unit area of glove per unit of time (e.g. mg/cm²/min)

5. INTRODUCTION

5.1. Background

The selection, use and limitations of gloves in the workplace to protect against chemicals infers that the user and glove provider know what glove to select for the task and how long the wearer can expect to be adequately protected. The situation is complex, but not so complex that most people can intuitively understand that a glove that is not visibly affected by a chemical or formulation is more likely to protect than one that shows signs of degradation. But given a selection of gloves that appear to work, how is a rational decision made to select the most appropriate. Commercial guidelines are, at the best, crude, and there is nothing to say about how tasks themselves will affect performance, nor is it possible to predict how a glove will perform with mixtures. The best advice that can be given at present is what gloves to avoid, not which gloves to select. What would be most desirable would be a way to predict the performance of gloves under stated usage conditions, so that selection is made knowing what protection is afforded.

5.1.1. Why measure?

Knowledge of how well a glove protects against a chemical is one of the factors which allows the appropriate choice of a glove. Other factors include which chemical (often a solvent), how long the glove is to be worn, tactility, tear resistance and cost. There is, as mentioned, little information about mixtures of chemicals or formulations. But *what* parameter(s) should be measured - and how?

5.1.2. Measure what?

The best test would give a single index which would directly relate to the degree of protection the glove actually gives the wearer. It would be difficult, but not impossible to measure the solvent permeation on a person. This could take the form of measuring the air inside a glove during use, or levels of the chemical (or a metabolite) in the body of the user, through blood, urine or exhaled air measurements. Biological monitoring would not differentiate the route of exposure, as inhaled (or even ingested) chemicals would add to the burden. Tests on gloves are usually performed in the laboratory, usually on new gloves, taking a sample from the palm. The indices used by manufacturers and published in journals include the moment that measurable amounts of chemical permeate (BT or LT), the rate at which it permeates (SSPR) and whether visible degradation has occurred. This project examines these indices and others suggested by other researchers.

The merits and disadvantages of the various indices will be discussed in detail in section Experimental Design, as computer software was developed to calculate these indices.

5.2. Work leading to this project

Two studies preceded this study and are reproduced in Appendix I. The first discusses the development of the Griffith Large Cell, which we consider a significant design breakthrough and the second is the proposal of a new permeation index which incorporated repeated solvent exposure into the index. These studies, and in particular the literature surveys which accompanied them, lead us to realise that there were many unanswered questions in the workplace performance of gloves.

6. AIMS

The stated aim of this study is to develop guidelines for the safe use of chemical gloves in the workplace.

This aim is ambitious, given the range of gloves, tasks and chemicals used in the workplace. The project could not hope to uncover all permutations, but in the process of systematically examining some aspects of glove use in the workplace, it was expected that the limited advice available on safe glove usage may be improved upon.

During the course of the project several existing guidelines were found and another two referred to in the literature. These guidelines have been considered in deciding the most relevant points to come from this study.

7. OBJECTIVES

The stated objectives of the project were to be able to answer the following questions:

1. *At what rate do the protective properties of chemical gloves change with actual workplace use?*
2. *What are the mechanisms of permeation and degradation and how does the pattern of exposure affect these changes.*

These objectives were found to be based on assumptions that did not hold up for the workplaces we visited. It was expected that gloves would be chosen for their performance, and that they would (like many other personal protective devices like ear muffs and respirators), be used for their full service life. We did not expect to find the primary reason for selection to be cost, and that for gloves to be disposed of after or during a single shift. The objectives above are then not realistic and the more generalised form of these objectives are appropriate for this study.

1. *How do the protective properties of chemical gloves change with actual workplace use?*
2. *What are the mechanisms of permeation and degradation and how does use affect these changes?*

Broader issues were addressed as the project progressed, arising from findings at each stage of the project.

8. LITERATURE REVIEW

This literature review started from a base using the work leading up to this project (Brooks, 1993) but was expanded and diversified from the gloves literature after the appointment of the project's Senior Research Assistant (Mr Fraser Smith) to the project. He was able to view the project from a polymer science and materials science viewpoint, something that most other researchers into glove performance had largely not appreciated.

The structure of this literature review allowed

- the development of the mechanical aspects of the glove testing facility, although the similarities between our approach and that of Jencen (1989) was a co-incidence;
- the critical analysis of other researcher's work, particularly in allied fields such as polymer science; and
- a review of the available advice on glove selection.

8.1. Sources of Information

Searches were performed on a number of databases to ensure adequate coverage of publications. These included:

- ASTI (CD-ROM)
- Chemical Abstracts (Online)
- NTIS (Online)
- RAPRA (Online)
- Science Citation Index (CD-ROM)
- Dissertation Abstracts (CD-ROM)
- Current Contents (Online)

The Online searches, except Current Contents, were performed by the Faculty Reference Librarian in consultation with one of us (FS). Some papers and all the PhD thesis had to be obtained from other libraries or overseas, with some wait.

8.2. Review of Literature

Only a few of the publications reviewed broadly covered the issues relating to glove permeation. These tended to be PhD theses which allow the space for lengthy reviews.

A study which preceded the present study (Brooks, 1993) was a crude attempt to develop an index which took into account re-exposure of the glove material. It is unique in that multiple re-exposures were performed. Anomalous trends were noted with the second re-exposure, after which a trend of increasing SSPR developed. An interesting linear relationship was shown between the mean of the inverse SSPR and the BT which shows that for a Nitrile glove exposed to toluene, a performance parameter independent of re-exposure could be applied.

A study undertaken for Jencen's PhD thesis (Jencen 1989) parallels much of our own work in the use of a computer to control an 8 channel test rig, but with a much lower degree of automation and data reduction.

Table 1 Comparison of this project with Jencen (1989)

Feature	Jencen	This project
Detector	GC, FID	PID
Cells	8	8
PC	XT 8087	486SX
Output	chart recorder, electronic integrator	computer files
Program	run on loading after background	prompt to load cell
Program	Turbo Basic	Visual Basic
Flow	mass flow transducer	mass flow transducer
Flow Control		metering valves
Output	qualitative, then quantitative	FTIR: both

Jencen (1989) appreciated the polymer science approach and the effects of temperature and thickness and used the oven from a gas chromatograph to set the measurement temperature.

Table 2 Effect of glove material on permeation

Parameter	BT	SSPR
Temp	-	+
Thickness	+	±
Crystallinity	+	-
Fillers (e.g. Carbon black)	+	-
Plasticisers (esp with PVC)	-	±
Polymer density	+	-
Cross-linking	+	-
Molecular size	+	-

The application of Thin Film theory to gloves could be of use and Jencen indicates the difference.

Table 3 Application of thin film theory to gloves

	Thin Film Theory	Gloves
Thickness (µm)	1-50	300
Fillers	n	sometimes
Plasticisers	no	sometimes
Pigments	no	often
Dyes	no	sometimes

Overall, a wide range of factors was investigated (thickness, temperature, mixtures), but with very limited application of statistics and no apparent statistical design or investigation of the physical mechanism of permeation. Nearly half the references in the bibliography were to polymer science. Little attempt was made to relate the findings to actual performance in the workplace. The use of three standard deviations above the background detector signal is better science than a BT determined from

the zero extrapolation of an open loop permeation curve, but it does make the BT experiment specific. Mention is made of quantifying the extraction of plasticisers by exposure to solvents, but these results appear to be missing from the thesis.

Nelson et al (1981) produced one of the seminal papers on the performance of polymer gloves. They examined 28 solvents and 28 gloves in a cell that is similar to the ISO cell. Different permeation curves are characterised and related to the permeation mechanisms, though the explanations lack insight into the actual mechanisms and permeant-polymer interactions. This aspect of the work has been widely referred to by other authors.

Olsen (1993) investigated the performance of examination gloves to micro-organisms. Even with penetration, some protection was afforded. Examination gloves are used widely in laboratories as chemical gloves due to their thinness and availability in convenient dispensers. This aspect of glove performance should not be neglected.

Perkins has been one of the major players in glove research. He has reviewed the interactions between solvents and glove polymers (Perkins 1993) and considers (Perkins 1988).

“all components in a written respirator program should also be used in CPC programs”

A major problem with trade secret additives, which limit the ability to predict glove performance, is outlined.

8.3. Guidelines for glove selection

There are a number of published guidelines in books (Raheel, 1994), specific rules (NSC in Appendix E), computer programs such as GloveES and compendiums such as the two volume “Guidelines for the Selection of Chemical Protective Clothing” published by the US consulting company Arthur D Little. The latter was not sourced during the project. The guidance can be specific - showing the best choices for a particular task using glove manufacturers brochures, Materials Safety Data Sheets (MSDS's) or computer programs such as GloveES; or broader, giving an understanding of the wider issues in selecting a glove such as given by Raheel (1994); or distinctly rule based such as the National Safety Council Guidelines (Appendix E). Standards such as AS 3765.1 1990 “Clothing for protection against hazardous chemicals. Part 1: Protection against general or specific chemicals” are a performance standard, but the appendices which form 2/3 of the bulk of the standard give guidance on testing, including permeation testing using an ISO type cell similar to that of Leinster (Leinster, 1986). The British Standard BS 7184 1989 “Selection, use and maintenance of chemical protective clothing” calls up similar performance standards and gives a flow diagram guided approaches to CPC, (with a brief mention of gloves) more from the point of view of the hazard rather than the performance of the CPC materials.

The approaches and their advantages and disadvantages are discussed below.

- **Professional understanding.** e.g. Raheel (1994)

This is probably the most desirable, but in practice it would not work except for an enthusiast or academic with a chemistry background. The mathematics, physics and chemistry give an understanding of the permeation processes, and the referencing to journal articles and books allows the reader to further research the problem in areas relevant to their own workplace. To apply a scientific approach would be very time consuming but should result in better understanding of the limitations that a particular glove selection will have on protecting a worker from chemicals in the workplace.

- **Manufacturer's brochures**

These are sometimes well formulated (Ansell, 4H) and simple enough for a person to avoid making the worst selections. They give very limited or no information on mixtures or how to de-rate the glove selected at elevated temperatures. If the 3-DSP for the gloves and the solvents listed was published, then a more rational approach could be made for selecting for mixtures and formulations, but a greater knowledge and training of the person doing the selection would be required. The selection of hearing protection has already seen this occur, with the better manufacturers publishing sound

attenuation at different frequencies, so that the noise levels at the ear for specific ear muffs or plugs can be estimated in a specific workplace

- **Material Safety Data Sheets**

Some MSDS's give specific guidance for the selection of gloves. Unfortunately this advice may be quite wrong, or refer to a glove which is very expensive or one which gives good protection but poor tactility. Potentially MSDS's are a good source of useful, product specific information. It is unlikely that specific permeation tests on gloves have actually been performed on most products, so the advice is not likely to be particularly good with anything but pure solvents. Formulations sometimes contain imported ingredients whose identities are poorly known, so it would be difficult for smaller manufacturers to give good advice on gloves. A systematic review glove recommendations in MSDS's could prove interesting.

- **Computer Programs**

Computer programs like *GlovES* purport to be expert systems, but they are really sophisticated lookup tables and a vast amount of published glove permeation data which try to emulate a professional occupational hygienist in selecting gloves for a task. *GlovES* does allow the selection of gloves using breakthrough times, permeation rates, tactility and tear resistance (based largely on thickness and whether they are supported). Selection for use with a second chemical may be made from the gloves selected, but not for a mixture of the chemicals. When the chemical is unlisted or not specifically known, the chemical group may be used to guide glove selection. There is a vast scope for using the 3-DSP in such a program to allow predictive selection, particularly with mixtures and formulations, to make allowances for skin or workplace temperatures, or even make estimates of transfer through the skin. The use of *GlovES* should be with caution - to guide to selection rather than to make the selection.

- **Rules for selection an use of gloves**

In Hassler's PhD thesis (Hassler, 1989) it is stated that the US National Safety Council Guidelines are

"the only official list of official rules which guide the selection and use of gloves".

We have not found any other set of rules, but they should not be used without some understanding of their limitations and omissions. These rules attempt to be comprehensive and obviously carry a lot of experience in their formulation, but they do not empower the rules as the underlying mechanisms are absent. There are some deficiencies -

- the advice on single agents (vs mixtures) does not make it clear that single agent has to be in the absence of a carrier solvent, as with some pesticides.
- the rules suggest a glove breakthrough time of 30 minutes in the absence of permeation data for chemicals with high systemic toxicity, but give no guidance on how to assess the breakthrough time.
- advice is given to "rinse gloves frequently" but the problems of using a solvent are not explained, though washing the outside with soap and water is suggested before reuse.
- decontamination is suggested when there are visible signs of absorption of toxic substances, but significant absorption of non visible amounts of the substance could occur.
- no mention is made of glove use at elevated temperatures

These are minor criticisms, but any rule based approach is inherently limited as knowledge increases.

8.4. Permeation Theory

There are interactions between the permeant (solvent) and the glove material, between the permeants in a formulation and the permeants and glove additives - such as leaching of plasticiser (Jencen 1989). These interactions make the performance of the permeation process anomalous and the interpretation of the results very difficult. A simple view is that the solvent diffuses through the non crystalline parts of a glove

8.4.1. Basic Concepts

For a chemical to enter the body, the most common routes are inhalation, ingestion and through the skin. The skin is usually the most exposed parts of the body that are protected - hands and forearms

(gloves), feet (boots) and front of the torso (aprons). The approaches to measuring permeation to any of these forms of chemical protective clothing (CPC) is the same, but it is usually the hands that are most exposed as the material has to be thinner for adequate tactility and the gloved hands are in direct contact with the chemical. The present approaches to measuring the performance of CPC is almost universally laboratory based on new gloves. Two principal indices are determined -

- the *time* it takes for measurable amounts to permeate the glove and
- the *rate* at which the chemical permeates.

The permeation through a glove may be considered in three stages (Schwope, 1988)

1. Absorption into the glove
2. Permeation through the glove material
3. Desorption on the inside of the glove

This simple model allows measurements to be made of glove performance and rank the performance of various gloves with chemicals. Interpretation of these rankings in the workplace is difficult as the skin may be in direct contact with the glove, be somewhat hotter than the work environment and sweaty, be flexing and only intermittently exposed to a mixture of chemicals.

8.5. Solubility Parameters

The concept of solubility parameters to predict the performance of gloves was first generally introduced to glove assessment by Perkins (Perkins, 1985). Three Dimensional Solubility Parameters (3-DSP) were first applied in the ink industry to determine the performance of solvents (Hansen 1988). Hansen outlined how the 3-DSP was developed and some of the limitations in its application to modelling the performance of gloves.

- **Dispersion (London) parameter**
Problems in solvents with chlorine or sulphur atoms or cyclic solvents
- **Hydrogen Bonding parameter**
This could be evaluated using infra red spectroscopy. A good estimate is to use 5000 cal/mol of the energy of evaporation to each alcohol group to obtain the this parameter
- **Polar Bonding parameter**
This parameter is due to the attraction of permanent dipoles in polar molecules.

The 3-DSP is shown to be not just an experimental figment, but to show real interactions between molecules.

The 3-DSP measures the forces on a molecule as the sum of dispersive, polar and hydrogen bonding forces - it shows how well the polymer dissolves in a solvent and is a representation of the distance between the polymer and the solvent in space. The further the distance, the less the solubility. This is effectually an analytic statement of the well known "*like dissolves like*".

Perkins (1985) reviewed the polymer chemistry concept of the 3-DSP to predict glove permeation, as it is not possible to measure every permutation of glove and solvent. The concept was extended to look at the solid polymers used in gloves, rather than solutions of solvent and polymer, by looking the weight gain of samples of glove immersed in solvent. This assumes that weight gain is inversely related to similarity of solvent and polymer, since "*like dissolves like*". The components of the 3-DSP - Dispersive forces (D), Polar forces (P) and Hydrogen Bonding forces (H) were juggled with a computer program to give the best (negative correlation) fit with weight gain. The values for ten gloves were given. Since the solubility parameters were from experiment, the effects of plasticisers and fillers are effectively included in the results. This could be used to eliminate the poor glove choices from potential selection, with a final glove selection depending on other factors such as mechanical properties of the glove and cost. For mixtures of solvents, weighted values of D, S and P are suggested. Perkins calls on glove manufacturers to publish product specific D, S and P values to allow complex selections to be made. Limitations in the approach as seen where the 3-DSP are not correctly determined and where molecular sizes and kinetic energy (temperature) are more important than solubility, and where cross linking of polymer strands constrains swelling (weight gain), but does

not greatly affect diffusion. This may be an over simplification, as Harogopad (1991) looked at the swelling of samples of engineering polymer membranes placed in solvents to determine the rate of diffusion from volume gains measured with vernier callipers and a micrometer. No quantitative relationship between size of the penetrant and chemical structure of the polymer could be found, but the functional group rather than molecular size appeared to be important

The effects of additives such as plasticisers and fillers makes the gloves less like homogeneous thin films (Jencen 1989) and is not yet accounted for in the use of this parameter. Jencen (1989) puts great faith in the capabilities of calculated three dimensional solubility parameters, provided the effects of plasticisers and polymer crystallinity can be accounted for and states:

“Continued refinement of these factors will improve prediction accuracy thus eliminating the need for individual evaluations of glove/solvent systems”.

This would however, still somewhat underestimate the complexity of the actual performance of glove in the workplace, where stresses and intermittent exposure occur, but it does point the way to the gradual evolution of realistic predictive models of glove performance.

Schwope (1988) in his ‘state-of-the-art’ review points to the lack of standardised testing procedures. He presents a theoretical discussion of open loop and closed loop systems and the effect of sample area and thickness which assumes new samples and Fickian diffusion. Lag times and the effect of detection limits as an index of breakthrough is discussed. The problem of having to calculate the integral for open loop testing and the effect of detection limit is not valid if permeation is detected in a time short compared with a work day and well before steady state conditions occur, as the amount of chemical permeating is small. No mention is made of use, statistics, sampling protocol or mixtures.

Hansen (1988) discusses Concentration Dependent Diffusion as being particularly applicable at low and moderate concentrations of solvent. Surface effects can be significant when the BT is short. For chlorobenzene challenging PVA (polyvinyl acetate), the variation is 9 orders of magnitude. Six orders of magnitude is graphically described as the difference between

“a snail crawling through the woods and a jet plane”

The effect of intermittent exposure on gloves, particularly ones where there is a deal of polymer solvent interaction, is not discussed, but the effect would have to be considerable, as sudden decreases in solvent concentration at the surface of the glove would dramatically reduce diffusion through the glove. Hansen notes the large effect of a small change in solubility for an exponential concentration dependence of permeation.

Table 4 Effect of solubility on models

Change in solubility	Fickian Diffusion	Exponential Model
1 to 4%	4 x	approx. 10 x

Where the glove did not dissolve in the solvent, little swelling occurred and the permeation (and penetration) process was thought to be dominated by the size and shape of the penetrant molecules.

Perkins (1986) did further work applying the 3-DSP to Viton and found an interaction of some solvents with plasticiser, an amine resin. There is a potential to predict performance, if the 3-DSP of both solvents and polymer plus additive are known.

8.6. Polymer Science

Aminabhavi (1988) reviews the mechanisms of diffusion through polymer membranes in a lengthy paper. A historical reference is made to the work of Graham who systematically looked at gas diffusion in rubber 150 years ago. The three models examined by Aminabhavi were

1. A **molecular relaxation model**, which accounts for swelling as the solvent content of the polymer increases and the non Fickian behaviour is described.

2. **Convection Diffusion** in glassy polymers. This is a two stage non-Fickian process controlled by swelling stresses.
3. **Differential Swelling Stress** caused by an uneven distribution of the solvent through the membrane.

He also looked at diffusion and sorption processes through polymer membranes (Aminabhavi 1991) and was able to classify the diffusion mechanisms into three classes according to the fit of the equation

$$Q_t/Q_m = kt^n$$

where Q_t is the “mol percent sorption”
 Q_m is the maximum mol percent sorption
 k is a constant
 t is time
 n is a constant described below which relates to the transport mechanism
 $n = 0.5$ is for simple Fickian diffusion
 $n = 0.51 - 0.75$ for non Fickian “anomalous” processes
 $n = 0.75 - 1.0$ for non Fickian concentration dependent processes.

The introduction of concentration dependent processes has immense implications for relating the performance of gloves in the workplace to the type of testing in the laboratory. As workplace exposure to chemicals is almost always intermittent, this highly non linear performance, particularly with gloves that perform poorly in laboratory tests, may greatly underestimate the actual degree of protection afforded in practice. Aminabhavi states that

“... a comprehensive treatment of the concentration dependence of diffusivity is an extremely difficult task”

The structural changes in membranes exposed to solvent using x-ray diffraction. was studied by Ghosh (1991). This technique and other standard techniques used in determining structural changes in polymers have the potential to be applied more widely in the study of glove performance. Lundy (1989) investigated the oxygen- nitrogen selective gas permeation properties of thin multi-layer polymer films. Scanning and transmission electron microscopy (SEM, TEM) were used to examine structure and porosity. Neogi (1986) investigated and reviewed the swelling of polymer membranes when exposed to a permeating solid and give a mathematical treatment of the process.

Stampfer (1988) looked at weight and volume changes in glove samples and related this to BT and SSPR and suggests it as a screening process. No detail is given on what gloves and solvents were used, so the fit of solvent - glove combinations which are known to give anomalous results could not be ascertained

8.7. Types of test cells

A number of cells for testing gloves have become popular, but the ones published in national standards - the ASTM and ISO cell are likely to predominate, despite their poor design.

8.7.1. ASTM

The ASTM cell (ASTM 1986) has become the reference cell of choice, but it has been modified by various users. Perkins (Perkins 1986) bored out the ports to allow a greater flow of air through the cell. Hassler (Hassler, 1989) used the cell in a horizontal position rather than the specified vertical position. The recommended use is with a sample in the vertical position to allow the challenge liquid to be one side and either a liquid or a gas to be on the collecting side. With a liquid, the pressures of the challenge and collecting liquids balance, leaving little mechanical distortion of the sample. The use of liquids - such as a simulated sweat solution of lactic acid, physiological saline and fats may be appealing, but it increases the complexity of the analysis and has shown to be of limited value. Liquids are also more difficult to analyse than gases in a flow through mode. Most of the papers referring to the use of this cell in the bibliography used a carrier gas - air, helium or nitrogen.

For this project minor modifications were made to the ASTM cell:

Table 5 Modifications to ASTM cell

	ASTM Cell	This project	Comment
Clamp	Stainless or Aluminium	Plastic (PVC)	Functionally the same, but better stress distribution to glass cell
Gasket	Specified	Not used	Used glove sample itself to act as gasket

ASTM F739-85 (ASTM 1986) is the main glove testing standard, against which other methodologies are validated. The method requires the use of a bulky, fragile glass cell and a sample some 60 mm in diameter, limiting the area of a glove from which a sample can be taken. Samples cannot physically be taken from anywhere but the back, palm or cuff of a glove for this type of cell. The method defines breakthrough time in terms of analytic detection limits, but this makes comparison between experimenters almost impossible, as a detector with infinite sensitivity would show an instantaneous breakthrough - a simple fact arising from the nature of diffusion. Worse, a detector with a poor detection limits will show a glove to perform better. It is just that the breakthrough is detected later. The method of determining the analytic detection limit is not specifically given, though this is often taken as three standard deviations of the background signal above the background. The length of the test is given as either the time till degradation, time till steady state conditions prevail or a maximum is reached. Exposure could be expected to reality to the area under an open loop permeation curve so if a maximum may be reached within a few minutes and then there could be a gross overestimation of the degree of permeation. There is no provision for re-testing, or any other testing which would tend to mimic the type of exposure found in the workplace. The requirement for only duplicate testing means that that the confidence intervals surrounding ranking of gloves is unknown but probably very wide. The method of bolting the glass halves of the cell together prescribes aluminium or stainless steel clamps, but this approach leaves little “give”, does not allow for non destructive testing (as a sample must be first cut from the glove to fit in the cell) and is it slow to assemble or disassemble. The requirement for temperature measurement is ambiguous. The obvious areas for temperature measurement are the exposed side of the glove and the inside side of the glove. The exposed side of the glove could be expected to be at a higher temperature if a carrier gas is used as there would be cooling from the latent heat of evaporation of the solvent from the surface of the glove. The approach is crude and time consuming and may account for the unfortunate lack of rigour in the testing protocol.

Another ASTM standard , ASTM F903-87 (ASTM 1987) is used to determine the resistance of CPC to penetration by liquids and is a far less sensitive test than the ASTM F739-85 test for permeation.

A number of researchers have used the ASTM cell but with some variations. Leinster (1986) calculated the BT graphically, but as a LT. He also considered the amount of solvent permeating in 30 and 60 minutes of use. These concepts, with 20 and 30 minute integrals, were adopted in this project. Flow of the carrier gas detecting permeation was scaled to sample area was suggested. Swelling by solvents (a mark of strong solvent polymer interaction) was investigated but no mechanism proposed. Samples were taken “at random”, a factor which should have been more tightly controlled, though the results were compensated for thickness. An appendix of the paper is almost identical to Appendix K of the Draft Australian Standard, the ISO cell method for glove permeation testing.

Perkins (1986) showed the disadvantage of Infra red Spectroscopy using Miran analysers to include the slow response time and the need to have high (5-10 lpm) flow rates which in turn produced undesirable pressures in a standard ASTM cell of up to 7.5 kPa (30” H₂O). The review of this paper made us decide not to use our own Miran analyser for routine testing as the slow, response times would have made it impossible to perform the required number of measurements on sequenced cells to properly characterise the permeation curve for each cell.

Mellstrom (1989) tested three permeation cells with a horizontal configuration of different size at different flow rates. Changes in BT with flow rate were not statistically significant. The cells were not validated against the ASTM cell. The SSPR was affected by flow rates (normalised to volume changes per minute. The statistical analysis was vague (e.g. “fits rather well to a logarithmic curve”) and ANOVA analysis is referred to, but there is no presentation of the statistics. Mellstrom does state that

flow rate (per cell volume) and flow pattern were crucial, but it is not clear how these conclusions were arrived at. None of the cells attempted to minimise collecting volume nor create good mixing by flow pattern design.

The cells used in our study had flow rates per cell volume well above that in this study, so we could be more confident of good mixing.

A range of other cells have been developed (Jencen 1989; Hassler 1989) up to the late 1980's, some for special purposes such as for looking at the permeation of solids (Fricker 1994). The disadvantage of using standardised cells such as the ASTM or ISO cell is that both designs are poor and improvements on the designs to produce a better, cheaper cell are inhibited. However it does mean that test results are more able to be compared.

8.8. Flow rates and carrier gas

The flow rate decided upon by Leinster (1986) was 25 volumes per minute, but he recognised that the rate should relate to the area of the glove sample under test, as this should determine the amount of solvent passing through the glove. The same flushing volume per unit area should give the same solvent vapour concentration in the carrier gas and so allow instrument choice and response to be standardised. The effect of a large cell volume would be to reduce the time resolution of the test setup, assuming mixing times are significant compared to instrument response times. It may be desirable to have a large dead space to contain solvent after mechanical failure of the test cell and this is evident with the ISO cell. Various flow rates have been used by others - 75 - 100 ml/min (Forsberg, 1986), 30 ml/min (Jencen, 1988, 1989), 500 ± 20 ml/min (Leinster, 1986), 60-120 ml/min (Mellstrom, 1989), 1000 ml/min (Vahdatj, 1989) and 555-3000 ml/min (Zellers, 1993). Fricker used a low 30 ml/min, but for testing permeation of solids.

Flow measurement during the permeation process has not been common, and bubble tube flow checks or rotameters appear to have been used.

In almost all experiments, the carrier gas was either helium or nitrogen, which are compatible with the use of gas chromatography. Liquids such as isotonic saline or simulated sweat have been shown to be of limited value, and have fallen from use.

8.9. Detectors

The detector of choice appears to be a gas chromatograph (GC), which limits easy automation of the process, particularly if a series of cells are to be measured in sequence. This has been usually coupled with a flame ionisation detector, but GC plus photo-ionisation detectors (Perkins 1986) and GC plus thermal conductivity (Vahdatj, 1989) have been used. Perkins (1989) used a Miran infra red detector, but found the response slow.

8.10. Thickness of gloves

Hassler (1989) considered that published differences in the performance (BT) between manufacturers is due mainly to variations in thickness, but does not present data to support this assertion. This difference means that a generic selection of gloves will give unknown degrees of protection. (The idea of correcting for thickness was considered for this project and the concept tried but found problematical for supported gloves)

Benzol (1993) found dexterity and mechanical damage were found to be inversely proportional to thickness, though learning how to perform tasks with gloves did compensate for loss of dexterity. This is important for chemical gloves, as BT are roughly proportional to the square of the thickness, and SSPR are roughly proportional to thickness. Benzol's data shows that the product of glove thickness and number of gloves mechanically damaged during testing is may be constant.

Table 6 Effect of glove thickness on damage

Thickness "T" mm	0.18	0.36	0.64
Number replaced "N"	73	25	16
N x T	13	9	10

8.11. Duration of tests

The duration of tests was variable but either 240 minutes or 480 minutes in most papers. Fricker (1992) used 620 minutes with his tests on permeation of solids. A working day could be considered 480 minutes, so it would be of more use if tests were performed until either 480 minutes or steady state permeation set in or the glove degraded. Permeation testing over a longer period would be interesting, particularly when the performance of mixtures is being compared with single agents, or where very toxic chemicals are used and a very high degree of protection is given.

8.12. Temperature and temperature control

Aithal (1990) looked at the permeation of aliphatic alcohols through polyurethane membranes at temperatures between 25 - 60 °C. There were only weak interactions between permeant and membrane, with no swelling or degradation, so the analysis was simple.

Zellers (1993) examined the temperature dependence of glove permeation by n-methylpyrrolidone NMP (a low vapour pressure solvent) using an ASTM-85 cell at temperatures between 25-50°C. High flow rates - up to 3000 ml/min were used with apparent pressure drops up to 750 Pa as the solvent had a saturation vapour pressure between 130 and 450 ppm, depending on the humidity. These high flow rates would not be needed with more volatile solvents like toluene. Modelling of permeation was done using 3-DSP in a similar way to Perkins (Perkins 1992) to be able to predict BT and SSPR at elevated temperatures. An alternative approach was made by application of an Arrhenius relationship to temperature using the solvent solubility and diffusion constant to estimate glove performance.

Re-exposure generally showed traces of the NMP on the inside of the glove material before re-exposure, though the levels were mostly below the analytic detection limit, so breakthrough was not considered to have occurred.

Zellers notes that the effects of elevated temperatures such as from vapour degreasing, may be significant:

“above 70 C even an incidental contact, such as a splash, at elevated temperatures can lead to rapid permeation”

An unsuccessful attempt was made to solve the diffusion equations developed by Zellers, so we cannot verify that his model is valid.

8.13. Replications and statistical analysis

The number of replications of a test gives the experimenter the ability to estimate the degree of variance in his test result. This is important when test results are compared, as a rational decision as to which glove to choose should depend on a knowledge of how reproducible the test data is. Is one glove really different from another? This is particularly important for the person buying gloves when the choice of gloves is limited and a chemical which permeates quickly. Is a large cost increase or stocking more glove types justified?

In most of the literature, the recommendations of the standards are followed with duplicate or sometimes triplicate testing (Leinster, 1986; Mellstrom 1989; Fricker 1992). Only Vadatj (1989) took four samples. Testing with the standard ASTM cell is very time consuming, but it does mean that there is limited validity in the results if comparisons are to be made with other results.

In none of the literature was the statistical significance of a difference between data discussed. A good approach would indicate the statistical (and thence rational) confidence that one should have that differences are real, usually 95%. Even better, and almost never mentioned in any paper, is the “power” of this assertion, which is strongly dependent on the number of tests performed and the variance of the test populations. This is usually taken at 80 or 90%, as data collected could randomly show or conceal real differences.

Mellstrom (1986) and Swaenegen (1990) use “t” tests, Olsen (1993) mentions “chi squared” tests, and Perkins (1986) mentions confidence intervals. There is great room for improvement.

8.14. Skin

The skin can be considered the ultimate inner glove, as it is a multi layer, complex bio-membrane separating the body from the environment. Chemicals may either have a local effect on the skin or be absorbed through the skin and have systemic effects. The combined protection of glove and skin has been little studied.

Jacobs (1993) examined the permeation of radio-labelled vapours and liquids through frozen pig skin. A significant difference - around a factor of two, was found between the phases. Such data could be useful in determining the actual route of adsorption in humans, where the solvent either is in direct contact with the skin or evaporates inside the glove before permeating the skin.

Leung and Perkins (1994) examined exposure to dioxins through gloves and compared an estimate of the skin uptake with that through inhalation. He found that (p 193)

“In most cases the absorption of vapours through the skin amounts to less than 10 percent of the total dose received from a combined skin and inhalation exposure”

An opportunity exists to measure the uptake of chemicals through gloves and the skin separately from lung uptake could be performed with stable isotopes of carbon and nitrogen or biological. Monitoring of the chemical or its metabolites or breath levels would be done using gloves set in a glove box exposed to the chemical in simulated workplace tasks. The real effects of use could then be examined but volunteers would be needed and the ethical considerations debated. This could give the first direct indication of the effectiveness of gloves in the workplace.

8.15. Mixtures of solvents and formulations

There is little commercial information on the performance of gloves with mixtures of solvents. The data from the 4-H glove guide (4H, 1990) below shows how, for two mixtures, the components do not permeate appreciably, but the mixtures can.

Table 7 4H glove guide - mixtures

Chemical	BT @ 21 °C (minutes)	BT @ 35 °C (minutes)
tert Butanol	>240	>240
Chloroform	>240	>240
Chloroform, tert Butanol 80:20	>240	8
MEK	>240	>240
Toluene	>240	>240
MEK, toluene 1:1	114	9

The 4H glove (4 hour) is a very thin laminate of three layers of polymers and displays remarkable permeation resistance to most chemicals. This glove and the similar North Silver Shield can be used as a near impermeable glove liner, for the glove is slippery and lacks abrasion resistance. It is important to note the large changes in chemical resistance to mixtures with temperature, as the temperature of the outside of the glove would be effectively skin temperature (around 33 - 35 °C) if it was used as a glove liner.

8.16. Decontamination of gloves

Laughlin (1994) reviewed the refurbishing pesticide contaminated CPC, but only in terms of removal of contaminants and with no mention of the effect on the protective properties of the CPC. Many of the materials referred to were fabrics rather than membranes and would be prone to penetration rather than permeation. Vahdatj (1989) examined the decontamination of CPC using an ASTM-85 cell. It was found that thermal decontamination of CPC was better than detergent and waster. However, temperatures over 100°C degraded the material. No attempt was made to use a vacuum to supplement a moderate temperature. Samples were taken from the palm and cuff, but there was no indication of

the variation of glove performance with position. Perkins (1987) examined four approaches to removal of solvent contamination of butyl chemical suits - air drying, oven drying at 50°C, freon and detergent. 3-DSP's were evaluated for the material and cleaning solvents. Large differences in the 3-DSP indicated a lack of need to decontaminate, though a difference of 10 for butyl rubber indicated a need for decontamination. It was found that air drying at 50°C was 100% effective. Perkins recommended hot soapy water for surface contamination, air drying at 50°C for matrix contamination. For low toxicity material use machine washing are suggested, but for laboratory testing is recommended to check the degree of decontamination (Perkins 1991).

Menke (1988) investigated butyl glove permeation and compared air drying at room temperature and vacuum oven reconditioning at 50°C overnight. Corresponding permeation rates were not given.

Table 8 Repeated Thermal Decontamination (Menke 1988)

	Thickness (mills)	BT 1 (min)	BT 2 (min)	BT 3 (min)	BT 4 (min)
Air dry	22.0	155	105	115	110
Oven 50°C	21.5	120	145	140	160
Vacuum 50°C	21.8	125	155	155	165

(From Menke 388 Table III 1988: butyl rubber with EGDME, ethylene glycol dimethyl ether)

Oven and vacuum drying are seen to produce similar results and to work better than air drying. Whether the more complex vacuum drying offers any advantages such as faster decontamination were not investigated.

8.17. Weight gain and swelling

Wu (1989) has developed an exact mathematical model to predict the effect of fibres and spheres in a polymer on swelling. This has the potential to applied to the effect of fillers in gloves as they are mechanically rather than chemically locked into the glove matrix. It is assumed that the sphere or fibre is unaffected by the solvent, a factor that may not be found in practice, particularly if the solvent leaches the plasticiser. This leaching makes the glove less flexible.

8.18. Use and re-exposure

Forsberg (1986) was one of the first to look at mixtures of solvents and to look at pre-exposed gloves "as a simulation of re-use". Thirteen liquids and thirteen gloves were tested A horizontal cell similar to the ASTM cell but smaller, was used. It was clamped together so that an intact glove could be tested. The samples were air dried at room temperature overnight and re-exposed. Forsberg found "no change in performance" with re-exposure.

Table 9 Re-use of Gloves (after Fosberg 1988)

Glove	Solvent	BT initial	BT reuse	SSPR initial (mg/m ² /h)	SSPR reuse (mg/m ² /h)	Thickne ss Initial	Thickness reuse
Butyl	Ethyl acetate>70% Ethanol	>4 h	>4 h	-	-	0.68	0.68
Butyl	Ethyl acetate>70% Acetone, Ethanol, Methanol	>4 h	>4 h	-	-	0.67	0.67
Butyl	MEK 30-70% Ethylene glycol acetate MIBK	>4 h	7	-	-	0.70	0.70
Butyl	Acetone <30% 2-methoxy ethanol <30% epoxy resin	>4 h	>4 h	-	-	0.65	0.65
Butyl	Toluene, Butyl alcohol Butyl acetate, Ethanol MEK, Xylene (all 5- 20%)	159 m	127 m	66	73	0.43	0.43
Nitrile	same	6 m	6 m	9150	7100	0.40	0.40
Nitrile	same	14 m	12 m	8410	7800	0.40	0.40
Viton	same	5 m	4 m	6700	7200	0.25	0.25
PVA	Toluene 30-70% MIBK Xylene <30% Epoxy resin	>4 h	>4 h	>4 h	-	-	-
PVA	Toluene 50% Xylene 50%	>4 h	>4 h	-	-	-	-

MEK Methyl ethyl ketone, MIBK Methyl isobutyl ketone; (data extracted from Forsberg 1988 Table III p191)

There was no statistical basis to reject a lack of change in the gloves with re-exposure, though with only duplicate or triplicate analysis, the confidence intervals for the data would be so wide as to very insensitive in accepting anything but the null hypothesis. 60% of the data shows a BT > 4 h, the testing time so the finding must be at least qualified to “no change within 4 hours”. Significant polar solvent interactions could be expected to show as changes in glove thickness through swelling though there is no evidence for this in this study.

Swedish Guidelines for the Selection of Chemical Protective Gloves are mentioned, but these documents were not sourced during the project, though it appears that these are an adoption of the recommendations of Schwöpe (Schwöpe 1988).

8.19. Solids

Fricker *et al* (1994) furthered their earlier work (Fricker 1992) looking at the permeation of nine organic solids through five types of gloves. Only two samples were used and the cell is reported as comparable to the ASTM85 cell. The experiments were performed with special unplasticised polymers which would contribute to the fundamental understanding of the behaviour of polymers but does not directly relate to the polymers used in gloves in the workplace. In addition, it was found that saline rather than nitrogen as the collecting medium made little difference to the BT or SSPR in most cases. In the anomalous case with unplasticised PVC they suggested that the saline occupied the available permeation sites, slowing the permeation of the solvent. It was noted that a very polar compound such as phenol would have increased permeability with such a polymer in its swollen state.

8.20. Workplace Observations

Holmes (1991) mentions the use of gloves on construction and industrial sites and found that for the application of epoxies, painters used gloves 68% of the time, but leather and cotton gloves were used rather than the polymer gloves recommended in the MSDS's.

Perkins (1989) looked at PCBs (polychlorinated biphenyls). The choice of glove - PVC - reported by Perkins, over much more expensive (Viton) gloves was experienced in this project. The PVC adsorbed onto cotton glove liners was analysed using a soils test for PCBs. Adequate protection was found, even though some permeation tests showed a BT of 30 seconds.

Raheel (1994) reviews the scope and application of CPC. A summary is made of the 1983 "Guidelines for the Selection of Chemical Protective Clothing" from Arthur D Little Inc

Rucker (1994) reviewed the literature on attitudes of pesticide workers to CPC. This area is not well reported in the industrial hygiene literature, yet the reasons for (not) wearing and caring for CPC are probably at least as important as the technical performance of the CPC.

Williams (1991) observed

"Only a minority of workers so far appear to be well informed on the causes and prevention of occupational dermatitis. For example, workers do not wear gloves unless they feel they absolutely must. When gloves are not worn, workers run the risk of becoming sensitised to potential allergens in the workplace. Among those who do not wear gloves, a significant proportion use gloves which are inadequate for the job, e.g. the use of cotton gloves for epoxies was reported"

Williams also noted that

"under the personal protection on the MSDS, specific glove recommendations generally require upgrading. Other available data from glove manufacturer's refer only to individual, pure chemicals, not formulated mixtures"

We developed the plan for this project with a number of invalid assumptions. One of these was that the reason workers would wear gloves was to protect themselves from the toxic effects of the chemicals. In one work place we were told that the main reason for wearing gloves was social - the workers did not like their hands to smell of solvents. The whole area of attitudes and comprehension of information supplied to workers is in need of more study.

9. GloveTest DEVELOPMENT

9.1. Initial approaches

The initial instrumentation strategy proposed in the submission for funds to Worksafe Australia was used as the basis for the instrumentation we developed during the course of the project. The initial design was a simple expansion on the setup already developed (Bromwich 1992), but with six channels, rather than the 8+ actually developed. The most innovative approaches were developed in the software, and this was continually refined throughout the project.

9.1.1. Initial design

The design below was submitted in the application for funding of the project.

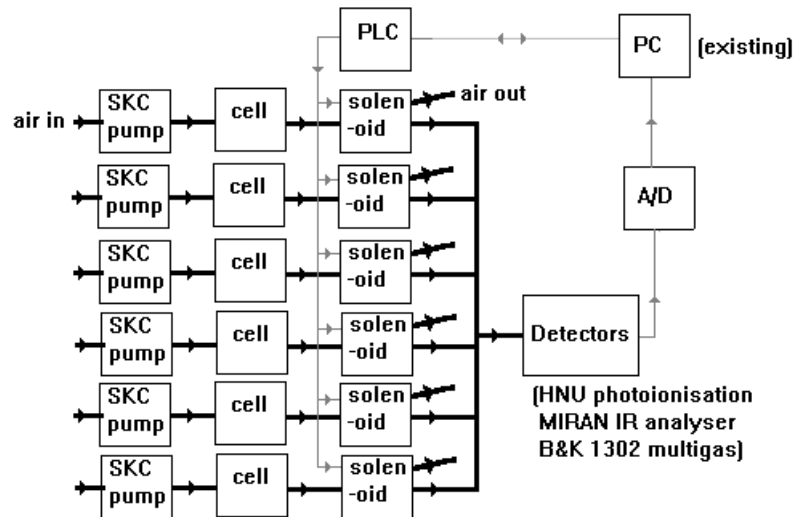


Figure 1 Nominal Test Rig Schematic

This design was to rely on six personal sampling pumps to pump air through the cells. The pumps would allow the flow rates to be controlled by the pumps. The output of the cells could be switched sequentially through a bank of detectors -

- a HNU photo ionisation detector,
- a Miran 1B Infra Red Analyser and
- a Bruel and Kjaer 1302 infra red multi gas analyser.

This arrangement would allow discrimination between components in solvent mixes. During the literature review it was found that Perkins (Perkins 1986) had used a Miran 1A Infra Red Analyser with a single cell setup and had found the response to the cell too slow due to the large sample volume inside the analyser. To have become dependent on the response time of the Miran would have meant too few samples from during a run, let alone a run which switched between cells. The Bruel and Kjaer was not used in the initial phase of the project - in fact money to buy additional infra red filters was used to buy a PC (see PLC), prompted by a huge rise in the quoted cost of the filter.

The figure below shows the actual schematic of the test rig for a standard run. It was modified for use with an intermittent cell; for calibration of the detector; and for validating the cells against an ASTM cell.

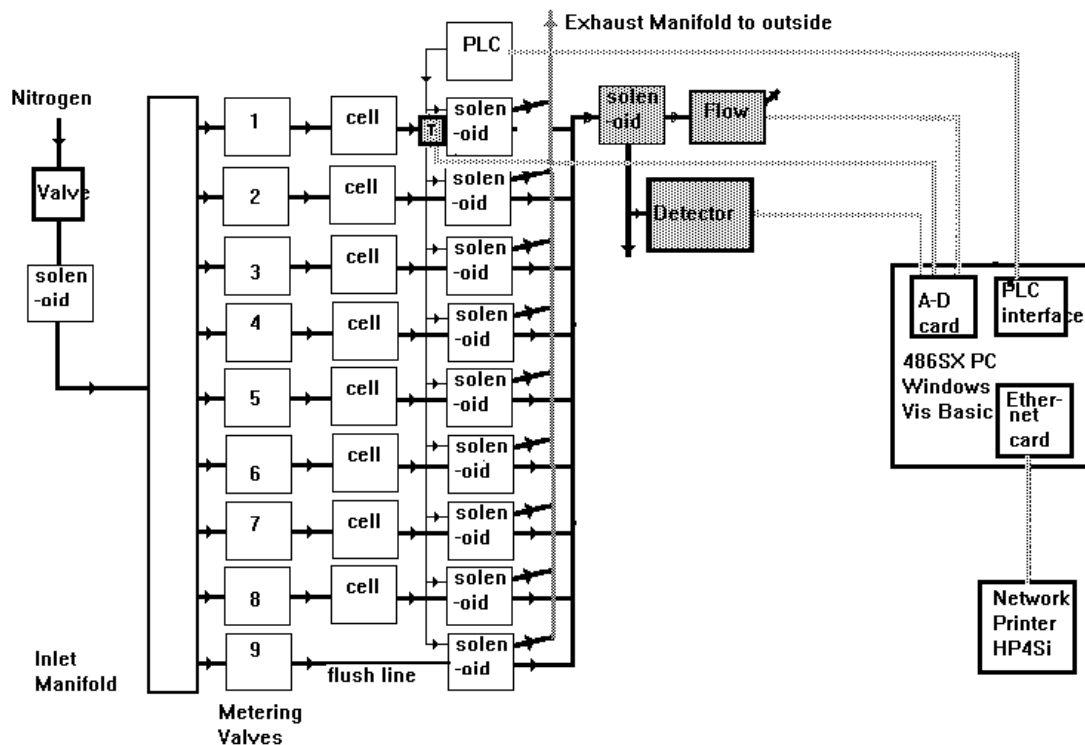


Figure 2 Actual Test Rig Schematic (Simplified)

The whole rig was mounted with screws and “Velcro” tape on a large board to keep it together and allow it to be easily moved. This proved invaluable when trials were performed using an Infra Red FTIR analyser in another building. In “Figure 3 Test rig on mounting board” below, the layout and the square conduit housing all the connecting wires can be seen.

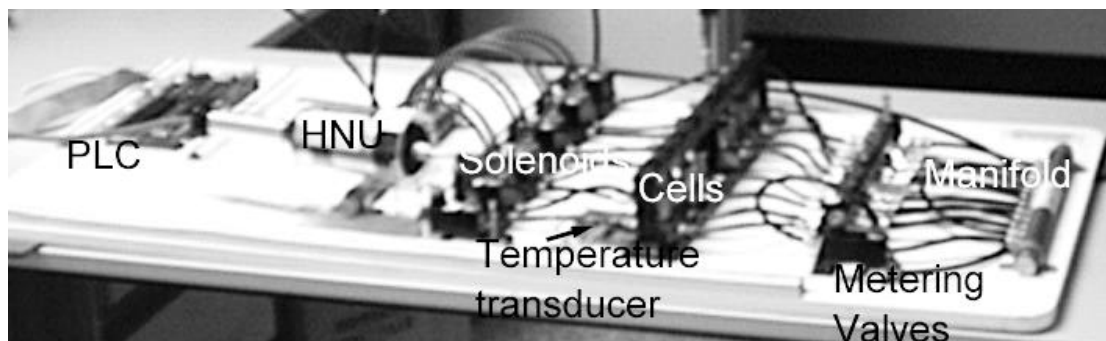


Figure 3 Test rig on mounting board

9.1.2. Carrier Gas and Flow Control

As constructed, the carrier gas was nitrogen rather than air, with flow control by metering valves attached to a manifold to ensure even pressure distribution. This ensured a high purity of carrier and removed potential carbon dioxide and water vapour infra red interferences from the flow. Eight channels - rather than the projected six, a flush line, plus an extra channel (not shown) for an additional experimental cell were used. The supply pressure at the manifold was much greater than the pressure at the cells, the flow through each metering valve was 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 during the pilot phase of the project was of bottles of nitrogen gas running out. As nitrogen usage was now precisely known, this became less common.

9.1.3. Flow Measurement

The flow past the detector was indirectly measured with a calibrated mass flow transducer (Microbridge AMW 3300) attached to the solenoid to the flow detector. This was only logged at intervals when the flow was diverted through it, avoiding excessive solvent exposure and allowing flushing flow rates in the collecting line switched by solenoid 9 from the cell solenoid blocks to be much greater than the rating of the flow transducer. The flow transducer output was calibrated with a Buck Calibrator on the output of the flow passing the detector and the calibration curve stored as a file. This calibration was deliberately indirect as it was the flow passing the detector, not the actual flow through the calibrator that was calibrated.

9.1.4. Solvent Detector

The project relied very heavily on the HNU 101 photo-ionisation detector which 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 detector gave a good compromise between sensitivity (the ability to measure a solvent) and selectivity (the ability to distinguish between solvents).

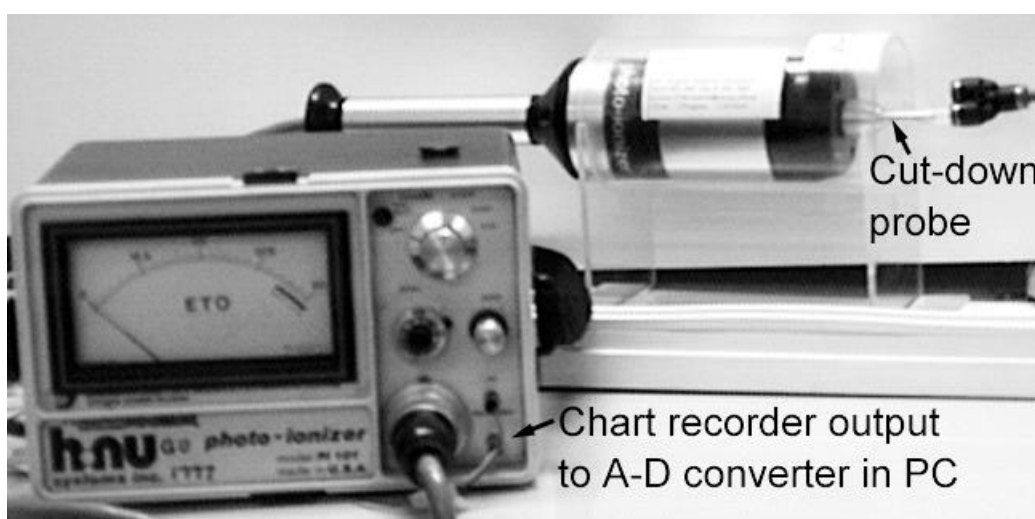


Figure 4 HNU photo-ionisation detector

The detector was modified by making a shorter inlet, rather than the standard 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 recorder analogue outputs were connected directly to an A-D card. It was found during the calibration that the instrument had a surprisingly linear response, even off scale on the instrument display.

9.1.5. Comparison between Proposed and Actual Rig Design

The table below shows the differences between the rig design proposed and funded and the rig actually built.

Table 10 Changes to Rig Design

Item	Proposed	Actual
Detector	HNU Miran 1B B&K 1302	HNU PE FTIR
Detector Calibration	Closed loop calibrator	Solvent in known volume in bag filled under computer control
Cell validation	Sequential runs	Special set up, in parallel
Carrier	Air	Nitrogen
Carrier regulator	SKC sampling pumps	Metering valves
PLC	Stand alone	PC + PLC card
Data storage	Single file from A-D	Files from PC
A-D	Single channel External	16 Channel, 12 bit Internal (inside PC)
Control Language	PLC control language	Visual Basic Professional v3.0
Control language modification	Modify in PC and download to PLC	Modify program in PC
Flow monitoring	Visual, plus bubble tube checks	Flow transducer, plus stored flow calibration data
Temperature monitoring	Manual thermometer	Temperature transducer, Logged temperature readings
Connectors	Forced push fit	Pressure connectors
Printer	9 pin dot matrix	9 pin dot matrix, then later a network laser printer

9.2. *GloveTest* Hardware

9.2.1. Overview of Instrument

The *GloveTest* rig operates on a relatively simple principle. Any solvent which permeates a membrane can be picked up in a carrier gas which 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 reaches saturation and for our flow rates, cells and choice of solvents, this was always so. The rig consists of eight 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.
6. Computer/PLC controller.
7. Software Control System (*GloveTest*).
8. Vacuum Drying Oven.

The specifications for the hardware are tabulated in “**Table 11 *GloveTest* Hardware**” below.

Table 11 *GloveTest* Hardware

Item	Description	Comments
Cells	Griffith Large Cell. Griffith Small Cell. ASTM Cell. Bromwich/Smith Intermittent exposure Cell.	All developed at Griffith University except the ASTM Cell.
Carrier Gas	High Purity Nitrogen	No IR interference
Carrier Gas Flow Rate	500 ± 10 ml/min	ASTM Standard Flow Rate
Experiment Time	180 to 240 minutes	User defined up to 16 hours is possible
Tubing	6 mm OD Nylon	Pneumatic tubing 2000 kPa burst Pressure
Connectors	Quick Fit tubing connectors	Festo and Parker
Flow Regulation	Fine Metering Valves 0.0005 CV Flow Co efficient	Set before each experiment using <i>GloveTest</i> software
Flow Meter Calibration	Done periodically using Buck Calibrator	Stored as a file in software
Flow Switching	Solenoid valves Festo	Controlled by PLC and software
Cycle time for 8 cells	~ 120 seconds	
Cycle time for one cell	~ 15 seconds	
Flush time	10 seconds @ ~ 5 litres/min nitrogen	Flushes out the measurement line made from the cell's solenoid bodies
Temperature Sensor	LM 355 Solid state temperature sensor	Output was 10 mV/degree Kelvin, measured on output line of cell 1
Solvents	AR Grade: Toluene, Hexane, Acetone, Methyl Ethyl Ketone, Methylene Chloride.	
Power Supply	<u>Solenoids</u> : 12V regulated supply external source. <u>Flow meter</u> : 10V regulated from PC off A/D card in PC. <u>PLC</u> : 5V from PC off PLC output card in PC	
Flow Rate detector	Honeywell mass flow transducer	Each cell's flow rate was logged during the experiment
Detector	HNU Photo ionisation detector Model PI 101	1-1000 ppm approx range

The items in the table above are discussed in more detail below.

9.2.2. Cells

Three types of cells were used for the glove experiments:

1. Griffith Large Cell.
2. Griffith Small Cell.
3. ASTM Cell.
4. Bromwich/Smith Intermittent Exposure Cell.

9.2.2.1. *The Griffith Large Cell*

This cell is very similar in design specifications to the ISO/Australian Standard 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 large 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 large 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 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 quicker than the ISO cell. The ISO cell in comparison is much larger than the Griffith large 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. Griffith large cell is able to be 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.

9.2.2.2. The Griffith Small Cell

This cell is a scaled down version of the large cell. This cell has a diameter of 9.5 mm and an effective exposure area of 71 mm². This cell uses the exact same clamping system as the large cell and was the cell most used for the testing done during this project. This has allowed 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 is attained. The smaller cells are also better aligned with the full scale response of the HNU photo-ionisation detector .

9.2.2.3. The Bromwich/Smith Intermittent Cell

An intermittent exposure cell was designed and constructed at Griffith University and is intended to mimic actual workplace exposure by a wetting and drying effect on the glove sample. The cell is the Griffith Large Cell which is inverted and sits on top of the intermittent exposure base. The cell is connected into the *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 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. A version of the intermittent cell has been designed based upon the Griffith Small Cell to fit into the Cell Clamp.

9.2.2.4. The ASTM cell

The ASTM cell was constructed of glass by *Labglass Pty Ltd*, a local company, to ASTM specifications (ASTM 1095). The ASTM specification had a glass stirrer, but this was not used as there would have been adequate turbulent mixing at the flow rates we used.

Table 12 Cell comparisons

Cell Type	Diameter (mm)	Area (cm ²)	Flow Required for same flow : area ratio
Griffith Large Cell	21.7	3.7	2608
Griffith Small Cell	9.5	0.71	500
ISO Cell	25	4.9	3462
ASTM Cell	44	15.2	10725

9.2.3. Programmable Logic Controller (PLC)

The PLC used in the *GloveTest* rig is manufacture by *ProCon Technology* (Australian) and is controlled directly from the PC via software. The software configuration will be explained later in the document. The PLC used has 16 controllable output devices of these 14 are 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 the A-D board below. Modifications to the code could be more rapidly achieved. The board chosen was Australian designed and made. The initial package we purchased had 8 output channels, a modified printer card which allowed bi-directional flow of information between the PLC and PC and some software and utilities.

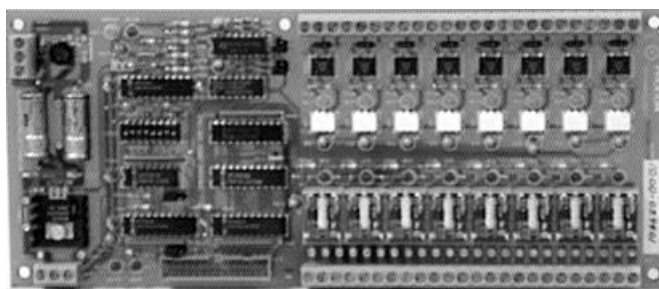


Figure 5 Eight Channel PLC

We quickly discovered that we would need more than 8 channels to control flow to the 8 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 transducer
- automatically switch off the nitrogen flow at the end of a run
- add extra lines for experimental cells

One choice would be to purchase a second card and daisy chain it with the first card, but we chose to buy a sixteen channel PLC card with a sufficient current capacity to switch the solenoids at a far cheaper price. This left spare capacity for adding extra cells or swapping channels on the PLC if and when a solenoid failed.

9.2.4. 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. See “**Figure 18 Griffith Large Cell**” and Bromwich 1992 in Appendix I. Ten were manufactured in the faculty workshop for use in an undergraduate experiment to determine the BT and SSPR of gloves.

A more compact design was needed for the rig and a steel frame developed. This had to be reinforced to prevent one clamp from loosening when another was tightened. Redesign and construction of this simple item took a lot longer than we expected.

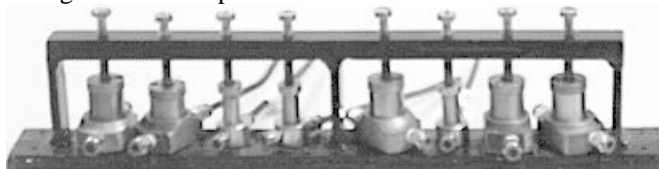


Figure 6 Cell Clamp for clamping Cells

It was found unnecessary to use a torque wrench to reproducibly clamp each cell together - a socket on a screwdriver like handle was quite adequate and a lot faster.

9.2.5. Solenoids

The solenoids to switch the flow to the detector were necessarily downstream from the cells as the cells had to be isolated absolutely from the detector except when they were being measured. This meant that any appreciable back pressure on the cells would be intolerable, as it would cause the glove cell to be pressurised and distort the sample. We sought a solenoid of the appropriate flow characteristics and “zero opening” pressure.

These were obtained from Festo (Model BNFH/2/3/M5). We were advised to get a certain model which had two solenoids - one to switch the flow to the detector and another to switch the flow to a dump line. Eight of these units were purchased.



Figure 7 Festo Solenoid

It was discovered the solenoids could be configured so that the flows were normally to the dump and when opened flowed to the detector, thus allowing two cells per solenoid block. Four solenoid blocks connected in a line to minimise dead space serviced eight cells. This permitted one solenoid block for flushing, one for the flow transducer/ solvent detector flow switching and one for the supply cut-off.

A generic 486SX Personal Computer was purchased to run the control software, house the A-D Converter, control the experiment with the PLC and store and print the data. Special ladder software (a special process software for sequencing the control of complex machines) came with the PLC and we attempted to convert it to run under Visual Basic, with little success. If this had been possible, then the PLC could have run in a “background” mode, but as the rate of sampling of the cells was very slow (seconds), the need to do this allowed us to use a cruder method of integrating the PLC control with direct addressing.

9.2.5.1. Network Connections

We shifted to a new building a few months into the project. The new building had ethernet connections, and to take advantage of the network printer, (a Hewlett Packard LJ4si,) a cheap network card was purchased. This also allowed the storage of files on the network server, so analysis of the data or changes to the control code could be done from any computer connected to the network.

9.2.6. The Flow Distribution and Regulation System.

The carrier gas, High Purity Nitrogen, attached to the flow distributing manifold at a pressure of ~400 kPa regulated from the gas bottle. The manifold unit was fabricated from a piece of brass pipe with a screw plug (brass plumbers type) at either end. The body of the distributor has 12 ports each with a 1/8” BSP (British Standard Pipe) Parker type quick connectors, rated to 1000 kPa. Because of the high incoming pressure the manifold the pressure to each cell was equal even if there was a slight bleed of gas from the system. The output ports were connected to flow regulating metering valves via 6 mm OD nylon tubing.

The flow metering valves had a very high flow coefficient from 0.0005 to 0.004 through 8-10 turns of the handle. The output pressure from these valves was effectively atmospheric and were easily regulated to produce a steady flow rate of 500 ml/min. This was to prove much more satisfactory than the proposed flow controls from a bank of personal sampling pumps.

9.2.7. Analogue to Digital Converter (A-D)

The initial plan was to purchase a single multimeter with an RS232 (serial) connection, to connect to a PC. For much the same price, we were able to purchase a 16 channel 12 bit A-D converter card. This allowed us to connect a number of instruments or transducers with analogue outputs. As a result we also purchased a mass flow transducer to keep a continuous check on flow rates of the carrier gas and made a temperature sensor to measure the temperature of the carrier gas as it left one of the cells (cell 1). 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 is manufactured in Taiwan.

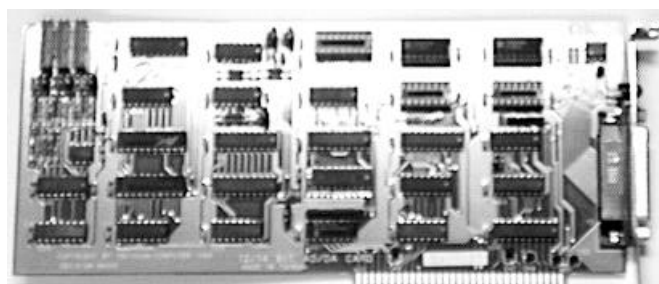


Figure 8 A-D Card (16 channel 12 bit)

The specifications of the A-D are summarised in Table 13 A-D Specifications below. The *GloveTest* rig uses 3 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 13 A-D Specifications

Digital to Analogue (not used in this project)	
Resolution	12 bits
Output Channels	Two One standard, One Optional
Output Voltages	
Unipolar Output	0-2.5V, 0-5V, 0-10V
Bipolar Output	0-2.5V, 0-5V, 0-10V
Conversion Time	Less than 2 μ sec
Output impedance	Load impedance larger than 2K.
Accuracy	1/2 LSB
temperature Coefficient	80 ppm/c
Analogue to Digital	
Resolution	12 bits ($2^{12} = 4096$)
Input Voltage range	
Unipolar	0-2.5V, 0-5V, 0-10V
Bipolar	0-2.5V, 0-5V, 0-10V
Conversion time	less than 28 μ sec per channel
Accuracy	1/2 LSB
Output Coding	Binary
Maximum input voltage	+ 12V
Channel Numbers	1. 16 channels : Single Ended Input 2. 8 Channels Differential Input
Temperature Coefficient	88 ppm/C

9.2.8. Computer*

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 board was equipped with a VESA Local bus and these type card were used for the IDE and Video controllers. 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.

* 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.

Figure 9 486SX personal computer

9.2.9. Detectors (HNU, Flow meter, Temperature)

Three detectors are used in the *GloveTest* rig and all are logged via the A-D and stored on disk. The detectors are described below:

- **HNU Photo-ionisation Detector**

This is a photo-ionisation detector initially used as a hand held detector for solvents. The HNU is able to use 3 UV lamps of 9.3 MeV, 10.2 MeV and 11.7 MeV. The lamp used for this project was the 10.2 MeV lamp. The HNU samples at a rate of 300 ml/min via an internal pump. The HNU has a range of 1-1000 ppm depending on how easily the solvent vapour is ionised. The output of this detector from a chart recorder output is fed into the A-D and the data is logged.

- **Microbridge Mass Flow Transducer**

To ensure that flows through each cell did not vary, a flow transducer was purchased. The best low cost transducer we could find was a mass flow transducer, but it did have limitations on its pressure rating.

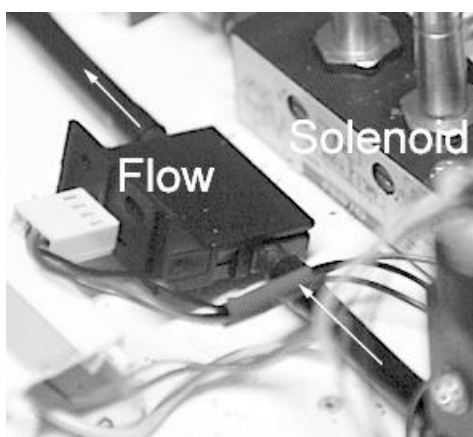


Figure 10 Mass Flow Transducer

The mass flow transducer is manufactured by Honeywell Limited and is one of their range of flow transducers. It has an operating flow rate from 50 ml/min to 1000 ml/min 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.

- **Temperature Sensor.**

A semiconductor temperature transducer (National Semiconductor LM 335 precision temperature sensor) as mounted in a piece of clear tubing in the line coming from cell 1 and the output was fed to the A-D card.



Figure 11 Temperature transducer

A trim potentiometer adjusted the offset. It has an output of 10 mV/°K and very high precision. The transducer was calibrated against a laboratory thermometer and was accurate to within $\pm 0.1^\circ\text{C}$.

9.2.10. Vacuum Drying Oven

This was constructed in house due to the need for a fast efficient method of drying the *GloveTest* cells and connecting tubing. To overcome this problem a very cheap and effective vacuum oven was developed, based on the only flat based, circular frypan available made by Kambrook. This was purchased stripped of its lid, and 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 $\pm 0.1^\circ\text{C}$.



Figure 12 Vacuum oven

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 standard method for connecting the Festo solenoids was with special pressure/ vacuum connectors with either Teflon or heavy nylon tubing. This allowed connection or disconnection to be made almost instantaneously. Consequently the airlines in the rig were connected to manifolds, valves, solenoids and cells with pressure connectors which not only gave perfect seals under pressure or vacuum with the nylon and Teflon lines, but could be instantly taken apart or joined. This allowed cells and lines to be quickly removed from the rig and baked between runs, but the butyl rubber seals were only rated to 60°C. Previously (Bromwich, 1992), the cells had been baked out at 105 °C between runs.

This vacuum oven allowed for very fast and effective decontamination of both cells and lines between runs and for less than \$100. A commercial vacuum oven would have cost at least \$3,000.

9.2.11. Voltage Regulators

A voltage regulator was constructed to ensure the correct voltage supplied the solenoids. 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 regulated power supply which had been adapted from an experiment requiring constant current charging of a lead acid battery at a high amperage.

9.3. Visual Basic and Programming

9.3.1. Initial Programming Approaches

Quick Basic - which is supplied with DOS (Microsoft Disk Operating System v 6.0), was investigated as the programming language to link the solenoid control with the PLC and the data acquisition. The language was supported by the PLC programming utilities, but lacked the structure and ability to provide a user interface, particularly in a graphical form. Visual Basic was available and the Software Developer's version was also available at a special educational price of \$130, which made it very attractive. It promised ease of programming, and as it operated under Microsoft Windows (Microsoft Windows for Workgroups v3.1), features like printing graphically would be easy. We had not counted on the length of the learning curve or the interfacing problems with the *GloveTest* rig when we made the decision, as we had made the PLC card work well under DOS. Fortran and Pascal were rejected as being too arcane and C was rejected as being too difficult.

9.3.2. Manuals and Programming Information

The manuals for Visual Basic were delivered three months after the software. Initially, a selection of manuals from other sources were purchased to bridge the gap, but these had limitations as they lacked technical depth. A huge (4 MB) computer "knowledge-base" was obtained via the Internet from

Microsoft and the Internet Visual Basic List Server subscribed to. This helped overcome some problems that had been solved by others. One request via the Internet (using the Visual Basic List Server) for help on obtaining a DLL for input-output commands returned two nearly identical replies from Iceland and Spain within four hours! Microsoft Visual Basic manuals were eventually borrowed from another user until our own arrived.

9.3.3. Visual Basic Pro

The Developer's version of Visual Basic (VB Pro v3.0) was chosen to develop the control language. Visual Basic is a powerful object orientated language which forces structure and modularisation of the programming code. It is 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. A number of applications such as Microsoft Money are written in VB and a subset of VB is now the macro programming language in all the Microsoft Office applications such as Word and Excel.

There was a long learning curve in discovering how to use this extremely powerful programming language, but the results were well worthwhile in terms of the fast changes to the code to enable sophisticated features to be added to the code - now named *GloveTest*, as the experiment progressed. It was quite stressful investing so much of the project time in developing a professional control program, particularly as the language and operating environment was so new, but our confidence in actually making it all work paid enormous dividends in the degree of automation and sophistication in the operational test rig.

9.3.4. Microsoft C

An attempt was made to develop a DLL (Dynamic Library Link) to operate the PLC using the programming Language C. This proved to be a difficult exercise and the method for scripting a DLL was not well documented in the C manuals. The attempt was abandoned.

9.3.5. MASM

A second attempt at writing DLL's was made with the purchase of MASM v 6.11, the Microsoft Assembler programming package. This was not successful, though the scripting of DLL's was better documented. Direct addressing to memory was eventually used to interface the PLC board to the Visual Basic control program. With a DLL it should have been possible to use the advanced ladder logic features of the PLC software which came with the PLC card

With a DLL to handle the PLC board, the programming would have been much more elegant, but a working solution had to be sought that worked as time was too valuable.

9.4. *GloveTest* Software

The following sections describe in outline the "*GloveTest*" control code which runs the experiment. 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 was written by one of us (FS) as the learning curve for fast code development was a long one.

9.4.1. Overview of Software

The software was written as seven major "forms" and had three procedural forms. The seven forms were:

1. Glove1
2. Glove2
3. Glove3
4. Comment
5. About
6. Analysis
7. Flowcal
8. STD

A brief description of each form is given below:

- Glove1:** This was the major form of the software and it is where most of the glove testing routines were activated.
- Glove2:** This form was for the testing of the flow rates through each cell and their adjustment before starting the experiment.
- Glove3:** This form was for the setting of the cell which were on or off during the experiment.
- Comment:** This form was used to put comments onto the data file like glove type position, solvent, and any other comment that the operator thought were needed. These comments were stored on the file header.
- Analysis:** This form was used to post process the data which was gathered by the instrument. This was used before or after an experiment.
- Flowcal:** This was for the calibration of the flow meter
- STD** This was for the experiment comparing the ASTM Cell and the Griffith Small and Large Cells.
- About:** This was a small “lead in” program which contained some information about the software and the programmer.

A number of “global variables” were defined to allow values to allowed in all modules after they had been set in one.

Table 14 *GloveTest* Program Global Variables

Variable	Type	Variable Description
Cell_1	integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_1=1) or OFF (Cell_1=0)
Cell_2	integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_2=1) or OFF (Cell_2=0)
Cell_3	integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_3=1) or OFF (Cell_3=0)
Cell_4	integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_4=1) or OFF (Cell_4=0)
Cell_5	Integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_5=1) or OFF (Cell_5=0)
Cell_6	Integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_6=1) or OFF (Cell_6=0)
Cell_7	Integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_7=1) or OFF (Cell_7=0)
Cell_8	Integer	This variable was really a Boolean type operator describing if a cell was ON (Cell_8=1) or OFF (Cell_8=0)
Exptime	Integer	This was the time that the experiment was to run for
Comment	String	This was the comment from the comment form and was place in the file header
Filename	String	This was the filename which all the data was saved to

9.4.1.1.Global Functions /Procedures

To allow information to be used in all modules, a number of global (cf. local) functions and procedures were developed.

Function: a_dconv(channel)

This function is for the analogue to digital (A-D) conversions and is a modified version of what is supplied with the card. The channel is passed to the function and the corresponding digital conversion is returned.

Function: Flow(a())

This function returns the flow meter reading in ml/min . The variable “a()” is an array containing the co-efficient of the polynomial calibration curve.

Function: Flowvalve (solnumber)

This function is used to turn on the solenoids required for a flow measurement to take place. The string value returned by this function is sent to the PLC via the PCIOXX TRS (Terminate Resident and Stay - a program element which remains in memory for use by other programs) driver.

Function: one_sol_on (sol)

This function returns the string value required to turn any one solenoid on.

Timedelay: (delttime)

This function is a wait timer in seconds, where the variable deltime is the required wait time.

9.4.2. Menu Selections

The hierarchical structure of the menus as they appear on the computer screen is shown below in Figure 13 *GloveTest* Menus. The most important items are in shaded boxes with heavy borders and the least important in plain boxes.

Error! Not a valid link.

Figure 13 *GloveTest* Menus

9.4.2.1. Menu: Experiment

This is the main menu for running the rig for normal testing and for the cell validation trials. The function of each is described below

Menu: Flush

This allows either the collecting line from the cell solenoids or the cells themselves to be flushed. This is particularly useful before a run 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)

Menu: Graph

This allows a graphical display of one or all of the cells (open loop curve, integral and carrier flow) and the ability to print the graph on a network laser printer.

Menu: Setup

This allows configuration to other than default values and calibrations to be performed and the calibrations to be stored.

Menu: Flow Calibration

This allows flows through cells to be checked and adjusted with the metering valves with a graphical and numeric display for each cell

Menu: Cell Setup

This permitted the cells to used to be pre-selected. This permitted any combination of cells to be used.

Menu: Photo-ionisation Detector

This allows a Tedlar bag (SKC) to be inflated for a known time (with millisecond accuracy) at a set flow rate from one of the metering valves. Typically 1 lpm for 4 min gives 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. All measurements in this project were reported in the same units as the HNU scale display as this was more convenient. Most of the work involved relative figures - the calibration just makes this figures absolute.

Menu: Settings

The base address of the PLC and A-D card can be set here. Personal preferences on the screen colour of the graphs can also be set.

Menu: Analysis

The Analysis menu was developed to reproducibly fit mathematically derived lines to those which 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.

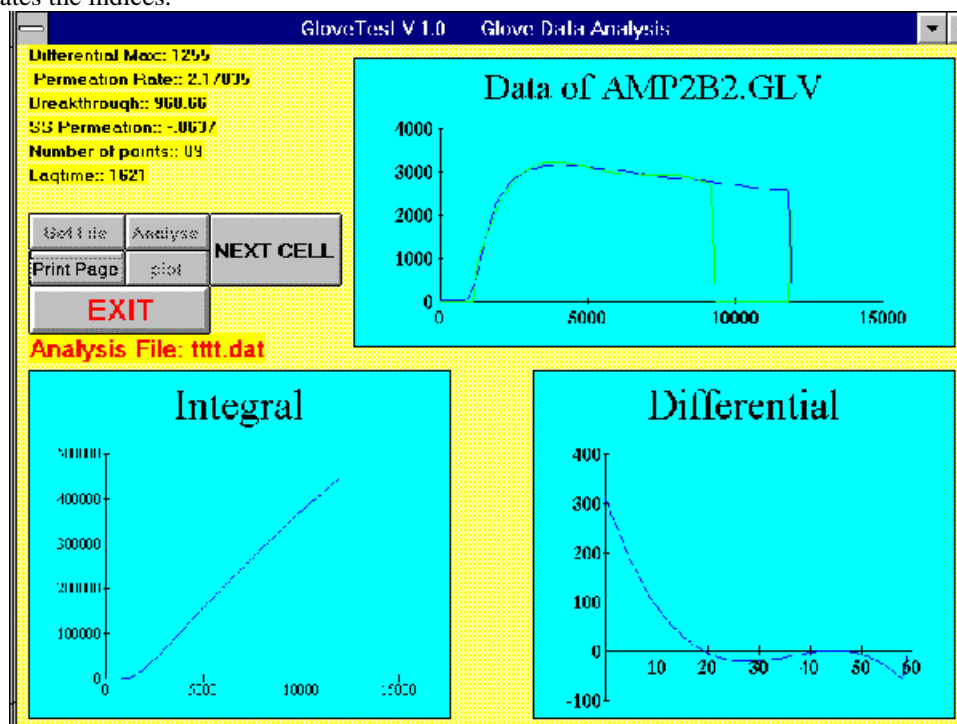


Figure 14 Screen for Analysis Module

9.4.3. Programming Structure

The structure of the *GloveTest* control program is shown in Figure 15 *GloveTest* Program Modules below. The more important modules are shaded and the support and housekeeping modules are unshaded

Figure 15 *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), VBXs (Visual Basic Extensions code) nor the Visual Basic environment itself.

The brief description below of the more important modules complements the Menu description above.

Form: Main Module

This is the main form to show the Menu and control the standard experiment.

Form: Data Analysis

This did the curve fitting and calculated the various indices for each cell.

Form: 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.

Form: Flow

Checking and calibration of the flow transducer

Form: Cell Validation

Cross calibration of the cells with the Standard ASTM cell

10. GloveTest TRIALS

10.1. Laboratory Trials

New gloves were trialled in the laboratory to thoroughly test the rig and prepare it for the Pilot Trials. It was found that the flow rates through the cells had to be increased to 500 ml/min, around the recommended rate 520 ± 20 ml/min for glove testing (AS3765.1, 1990). Fortuitously, this was also the optimal flow rate for the HNU photo-ionisation detector and kept the output of the meter on scale.

Operational factors were modified. These included:

- Strengthening of the frame holding the cells,
- Addition of a cut-off solenoid for the nitrogen carrier gas to stop wastage at the end of a run (a major problem with overnight runs)
- Determining the best way to reproducibly tighten the clamping bolt on the cells. A torque wrench was tried, but it was found that a socket wrench on a screwdriver like handle worked best.
- Developing a fast connect - disconnect system for the cells and other plumbing.
- Developing a vacuum oven to allow rapid decontamination of cells and gas lines wet by solvent during runs. The seals on the connectors mentioned above were only rated to 60 °C, so a fast, cheap method had to be developed.
- Developing of a protocol and method of recording of what we did and how we did it. This continually evolved throughout the project.

Thirteen indices were developed based on those proposed in the literature, and some of our own. The indices we recorded for each run were all determined mathematically from the permeation curves through selecting a point on the curve by its value (e.g. Max Point) and recording the corresponding time (e.g. Max Time), but using the calculated differential (slope) or integral (area) of the permeation curve, with fitted polynomials to the critical part of the curve to reduce “noise” effects. This ensured absolute repeatability, objectivity and automation to an otherwise tedious process

1. **Mid PointTime** This is the time taken for the permeation curve to reach half its maximum value. As this point could be determined quite precisely, we thought it may be interesting to correlate its values with Break Through Time and Lag Time.
2. **Mid PointValue** This is the response (A-D value between 0 and 4095) at the Mid Point Time.
3. **Slope** This is the Slope of the permeation curve at the Mid Point Time. It was determined by taking several points each side of the Mid Point Value and calculating a line of best fit through it (to intercept the time axis at the Break Through Time and the response axis at the negative Intercept value)
4. **Intercept** This is the intercept on the Response Axis, and for a run performing properly, it is always negative. This parameter proved useful in discarding data which were gross outliers, as a positive value had no meaning.
5. **Break-Through** This is the time intercept of the Slope line. This has been produced manually by other researchers. The ASTM-85 method suggests a time when the signal can be discriminated from the background, but this is of little use in practice as it is totally experiment dependent.
6. **Max Point** This is the maximum response or permeation rate.
7. **Max Time** This is the time at the Max Point, found by differentiating the permeation curve, fitting a polynomial to it and determining the time at which was zero (the slope was flat)
8. **Top Slope** This was determined by determining the slope at the Max Time
9. **Top Intercept** This is the intercept with the Response axis by the Top Slope line
10. **Steady State Permeation Rate.** This is the slope of the integral of the permeation curve at the Max Time, calculated in the same way as the Slope
11. **Lag Time** This is the time intercept of the Steady State Permeation Rate line
12. **Integral 20 min** This is the area under the permeation curve 20 minutes from application of the solvent. It effectively is an index of the amount of solvent permeating the glove in 20 minutes.
13. **Integral 30 min** This is the same as the 20 minutes integral, but for 30 minutes.

10.1.1. Choice of solvent/ detector

The chemicals in the ASTM F1001 1986 Standard Guide for Selection of Chemicals to Evaluate Protective Clothing Materials and the response of the three detectors we had are listed in “Table 15 Detector Characteristics” below, along with the detection limit for the B&K 1302 and the Miran 1B. The detection limit for the HNU 101 was not given in the literature, but was adequate for the testing in this project. The HNU at full scale read about 1 mg/m³ (see Calibration). which corresponded to about 3000 units on the 0-4095 scale of the A-D. An offset of 10 was built into the A-D converter and the sensitivity was about 5, corresponding to 1/3000 = 0.0003 mg/m³ for toluene.

Table 15 Detector Characteristics

Group	Example	HNU 101	B&K 1302	Miran 1B
		10.2 eV lamp	filter	DL*
Ketone	acetone	✓	970, 977, 987	DL* 0.1 0.6
Nitrile	acetonitrile	✓	936, 974	5-10 7.6
sulphur compound	carbon disulphide	✓	984, 985	1 4.8
Chlorinated paraffin	dichloromethane	✓	974	0.1 0.4
Amine	diethylamine	✓	972	1.1 1.1
Amide	dimethylformamide	✓	973	0.2 0.2
Ester	ethyl acetate	✓	969, 974, 987	0.08 (0.015) 0.07
Saturated hydrocarbon	n-hexane	✓	987	0.015 0.1
1° alcohol	methanol	✗	936, 974, 987	0.04 0.3
Nitro	nitrobenzene	✓	978	0.9 0.9
Inorganic base	sodium hydroxide	✗	✗	✗ ✗
Inorganic acid	sulphuric acid	✗	✗	✗ ✗
Chlorinated olefin	tetrachlorethylene	✓	977	0.06 0.08
Heterocyclic Ether	tetrahydrofuran	✓	973, 974, 981, 987	0.03 0.2
Aromatic hydrocarbon	toluene	✓	981, 987	0.04 1.1

DL* detection limit in ppm, B&K filter in bold is the one of choice

10.2. Calibration

• HNU Photo-ionisation Detector

The main detector for the project was a HNU 101 photoionisation detector with a 10.2 eV lamp connected to a channel of a 12 bit A-D converter in a PC. The scale reading of the instrument was not recorded, as the A-D logging of the instrument’s output was more accurate and precise than a reading from an analogue scale. The scale did provide an indication in addition to the graphical display provided by the *GloveTest* software that the experiment was performing properly. See Appendix D for manufacturers details of the response of the detector to various solvents.

The calibration of the was crucial in determining the absolute determination of the various permeation indices. To create an atmosphere with known amounts of solvent, a Tedlar bag (SKC) was inflated with 4 litres of nitrogen gas using the *GloveTest* apparatus to perform a timed fill with millisecond accuracy. The flow rate was determined with a Buck Calibrator. Between 0 and 4 microlitres of solvent (toluene) was introduced into the bag on successive runs through the connecting tubing with a Hamilton micro syringe directly into the bag through the connecting plastic tubing. The time, date, amount injected and the response of the A-D converter were automatically logged to a file for analysis. The bag was evacuated with a vacuum and flushed several times with nitrogen between runs,

removing all detectable solvent from the bag. “Figure 16 Photoionisation detector calibration” below shows the response of the detector

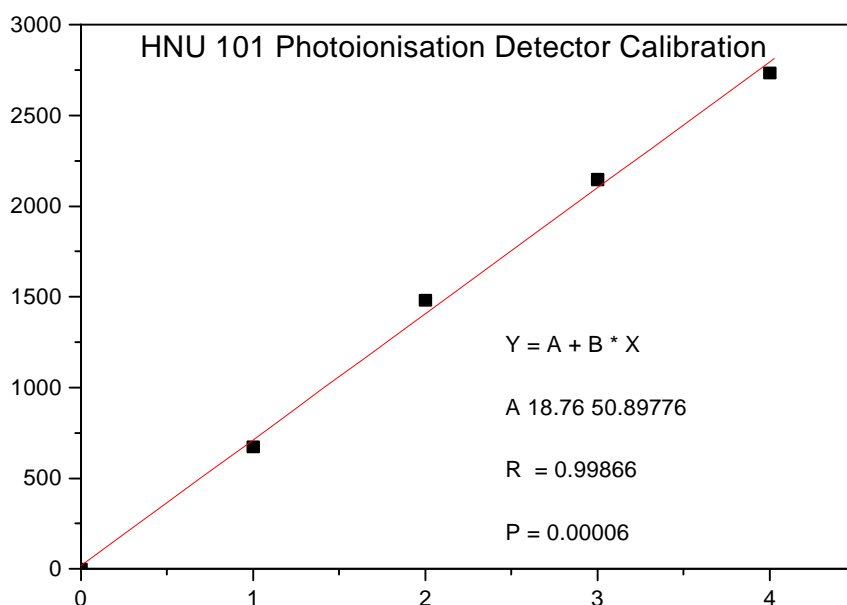


Figure 16 Photoionisation detector calibration

The figure clearly shows a very linear relationship between the amount injected and the response of the detector. The analogue signal from the detector is still linear when it displayed as off-scale on the instrument, validating the use of the A-D converter for measuring glove permeation. The calibration of the A-D response of the detector signal for toluene is $1 \text{ mg/m}^3 \text{ toluene} = 3224$, assuming density of 0.867 for toluene. Thus full scale of the A-D response for toluene is roughly 1 mg/m^3 .

10.2.1. ASTM Cell

The ASTM85 cell is accepted internationally as the standard cell for glove testing. No development in cells would be complete without demonstrating that the new cell was comparable with the ASTM cell. Detailed drawing of the cell were available in ASTM F739-85 (ASTM 1986) and a cell was manufactured by a local company Labglass.



Figure 17 ASTM Cell

The cell is large, unwieldy and would require around 10 lpm of air flushing through the cell or diluting the effluent air for most solvents using the photoionisation detector we were using.

10.2.2. Griffith Large Cell

This was initially developed for teaching purposes and is described in Bromwich 1992 (Appendix I). It bears a striking resemblance to the ISO Cell in AS 3765.1 (AS 1990) which was unknown to us at the time of its development.

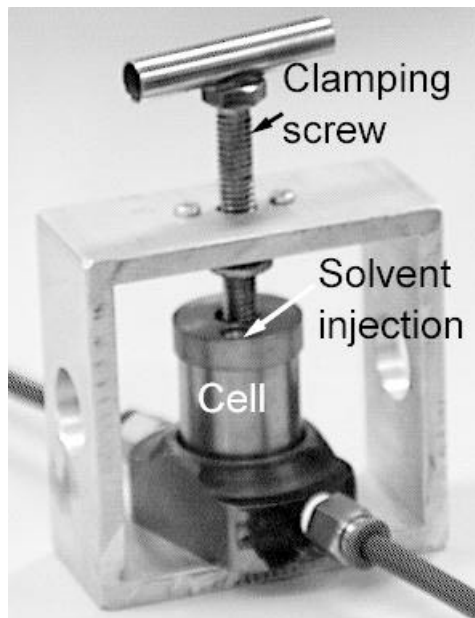


Figure 18 Griffith Large Cell

It is superior to the ISO cell in that the cell

- is simpler to construct,
- is faster to assemble or disassemble (one versus four bolts)
- requires less sample preparation (wad punch rather than elaborate template)
- can use a smaller sample (with similar exposed area)
- has a smaller dead-space
- can sit on a flat surface
- can measure in-situ without destroying the glove

10.2.3. Griffith Small Cell

This is a development from the Griffith Large Cell, but using a sample 9.5 mm across rather than 21.7 mm across. The choice was made from the selection of stock stainless steel section for the cell walls. This size allowed better matching of the response of the detector to the amount of solvent permeating and a biopsy technique to the fingers of the glove.



Figure 19 Griffith Small Cell

Measurements at different parts of the glove had not been investigated before. The cells were also cheaper to make as they used less material.

10.3. Cell Validation



Figure 20 Validation of Griffith Cells

Validation of the Griffith cells required the comparison in parallel between them and the ASTM cell. To produce the required flow rate through the cells to keep the detector from going off scale, flow rates proportional to the exposed areas of the cells were calculated. See “Table 12 Cell comparisons” on page 28 To obtain these flow rates in practice without unduly pressurising the larger cells or the photoionisation detector, diluting carrier gas was added in a special mixing chamber in a line just before the photoionisation detector. It took three trials of chamber to produce adequate mixing and a small dead volume. Mixing Chamber 3 in “Figure 21 Mixing Chambers” below was the one that was finally used.

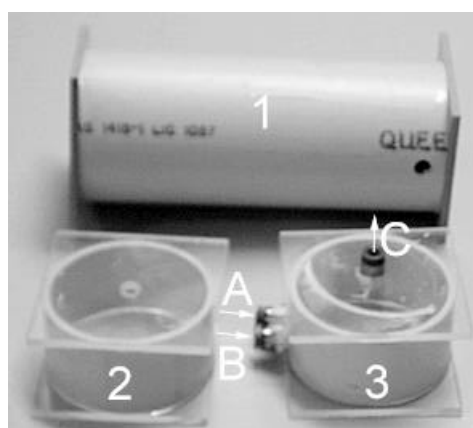


Figure 21 Mixing Chambers

The first chamber (1) was too large, the second (2) gave insufficient mixing and the third (3), by the addition of an internal baffle, gave the desired amount of mixing. The cell effluent enters at “A”, diluting nitrogen at “B” and the mixture swirls in the chamber and exits at “C” to be sampled by the photoionisation detector.

A significant problem that dogged the project was the intermittent failure of solenoids on the PLC board controlling the switching of valves and nitrogen gas running out. The figure below showing the flow to three cells illustrates the problem. Data points corresponding to the flows where the flow has changed or the gas has run out have been ignored in these validation studies.

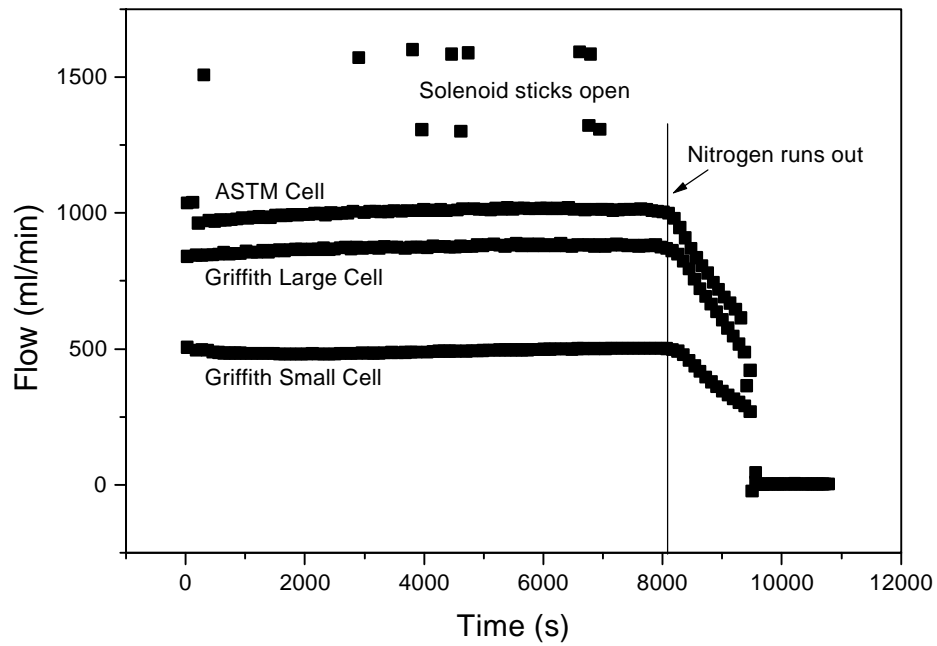


Figure 22 Gas supply and solenoid problems

An illustration of the cell responses from run F-2 challenging PVC with toluene is shown in the figure below. Adjustment for flows did not align the curves, so only partial validation was achieved. An undetected arithmetic error is suspected, and the validation trials will be repeated in continuing work to permit the publication of much of the project's data.

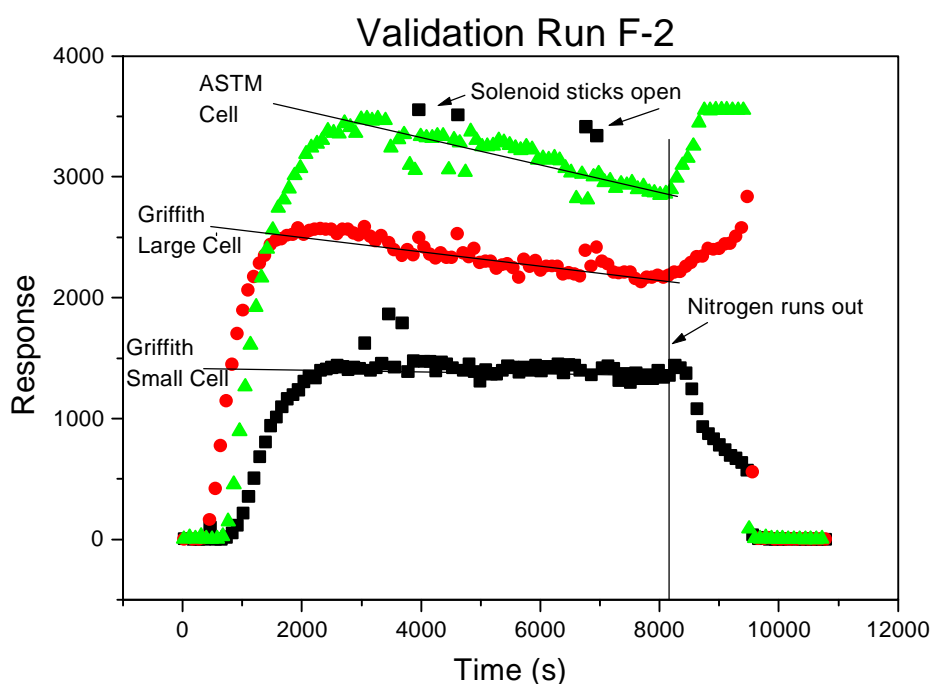


Figure 23 Run F-2 Cell Validation

A definite ratio exists between the cells, but the Griffith Small cell shows a flatter steady state response. The Griffith Large Cell and the ASTM cell both show an earlier breakthrough time and a decline after the maximum permeation is reached. This may be related to the greater ability of the larger samples to swell and distort as the Griffith Small Cell glove sample is mechanically more constrained.

10.4. Pilot Trials

The Pilot Trials was designed to test our approaches in the field and to look at gloves that had been used. The principal aim of this phase was to determine the number of tests that would be required to statistically differentiate “new” from “used” gloves - assuming that such a difference did exist. This was more difficult than we expected as the sophistication of the test software allowed very precise and reproducible mathematical extraction of performance indices, rather than manual graphical estimations most other researchers have used. Rather than just choose from BT or SSPR, we now had an array of performance data to choose from. We also had no guidance from other researchers as they all used an arbitrary duplication or occasionally triplicate analysis which had little or no statistical basis for determining whether differences between sets of data were real or random. The simple aim of determining how many runs was needed changed into an examination of what these extra parameters meant, particularly how they correlated with each other.

The development of a small version of our cell, the Griffith Small Cell, allowed us to take samples from any part of the glove, including the fingers, effectively allowing a biopsy approach. An additional parameter which then we introduced during this phase was the recording of the position of the sample from the glove - fingers, palm or cuff (5 positions), and front or back, a total of ten positions. This approach appears to have not been done before, but it somewhat increased the complexity of our data analysis as we found that “position” was at least as important as “use”.

The site for our Pilot Trials was a solvent recovery operation. The range of solvents is shown in “Table 20 Chemicals used at Pilot Trials site” on page 54.

Another factor we had not expected was that the gloves were not selected for their chemical performance but cost, and a facial tissue (“Kleenex”) approach to gloves was taken. Gloves were

simply replaced as soon as the degree of degradation was unacceptable. Gloves were never worn a second day as the users did not like to put on smelly gloves. This experience was re-enforced during the main part of the study. This did mean that the trials to determine the rate of change of performance by taking samples at intervals up to the life of the glove were a little meaningless, at least for the type of workplace we selected. Consequently the degree of use become “new” or “used” to determine whether there was a significant difference, particularly when the exposure to solvents was intermittent. At this stage, our literature review was also beginning to uncover information on concentration dependent diffusion, a factor not investigated by other glove researchers.

We were able to make estimates of the number of gloves we should test to determine a real change in performance, but the total number of tests per glove had blown out by a factor of ten due to our investigations of the effect of “position” from which the sample was taken.

We did consider doubling the number of cells, but the project budget would have been too stretched by the cost of the metering valves and extra solenoids. The fast response of the HNU photoionisation detector would have been adequate to service 16 cells and we now had the reserve PLC capacity though the addition of an extra 16 channel PLC card to switch all the solenoids controlling the gas flow through the cells.

A decision was made to not measure thickness as it was time consuming and the measurement would be difficult to interpret with supported gloves. The thickness of the polymer component of the glove would be indeterminate as its penetration into the supporting fabric could be expected to be very variable. The figure below expresses the problems we saw.

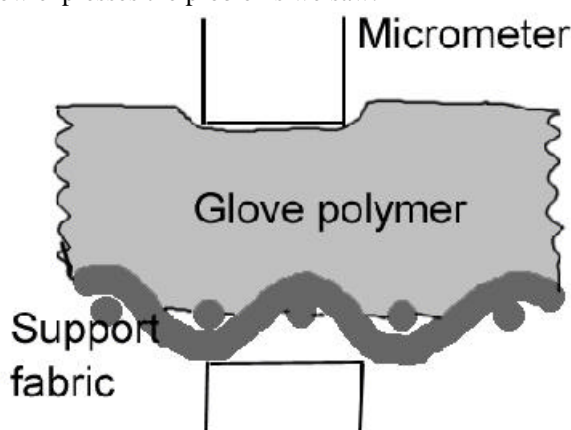


Figure 24 Measuring glove thickness

The micrometer anvil would tend to indent the polymer; the degree of penetration of the support fabric would be very variable. the polymer surface is rough (and with cheap gloves, inhomogeneous regions and inclusions are obvious). Mechanical measurements of thickness could only give a coarse indication of true polymer thickness. Non mechanical testing such as beta radiation attenuation may provide a better measure of thickness.

This would still be regretted, as it may still have allowed some indication how much of the variation of glove performance with “position” could be explained by variations of thickness. Weight before and after exposure for each glove could also have been made, as the Occupational Hygiene laboratories acquired a Sartorius M5 microbalance ($5\text{ g} \pm 1\ \mu\text{g}$ accuracy) from the National Quality Rounds during the year. A small experiment to determine the degree of variability of sample weight and thickness with “position” was performed to indicate trends. As all the samples were labelled and wrapped in aluminium foil and stored in bags, it will be possible to retrospectively estimate these data.

10.5. Main Trials

The Main Trials was launched by extending the survey to a number of other workplaces in industries we expected to be heavy users of solvents - petrochemical and paint industries. The factors we would investigate were

- glove type

- solvent
- position
- glove use

using the thirteen performance parameters we had developed in the *GloveTest* software.

Reaching this stage of the project took a lot longer than we expected due to the long *GloveTest* rig development times, the discovery that “position” was so important and unforeseen delays in obtaining parts and equipment failure.

10.6. Intermittent Cell

A modification of the Griffith Large Cell was made to try to simulate the intermittent nature of glove exposure in the workplace. Leinster (Leinster 1986) stated

“it is not possible to mimic the variety of exposure conditions that occur in practice”

but we have developed a cell which can reproducibly simulate almost any pattern of intermittent exposure that occurs in the workplace under computer control. A number of designs were considered and trials were made using a car windscreen washer motor and a discarded intensive care syringe injector. Simple gravimetric feeds were also considered until the present design evolved. Time did not allow us to fully investigate this factor, but this will be more fully investigated in the future.

A simpler, smaller intermittent exposure cell based on the Griffith Small Cell has also been designed but not yet constructed, to allow up to eight measurements to be made at once, so that the variability in this factor can be systematically investigated.

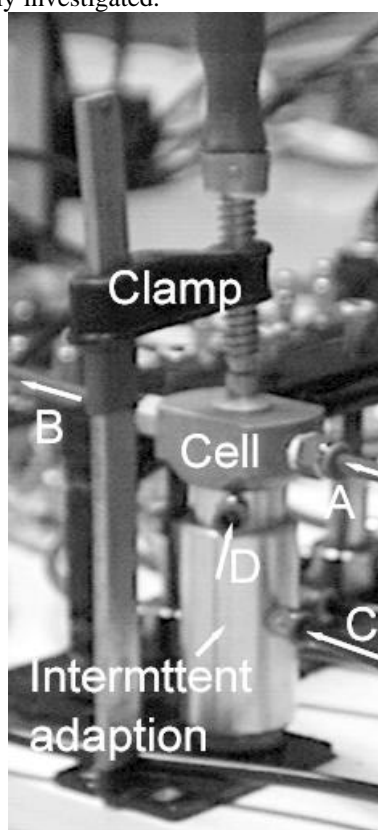


Figure 25 Intermittent Cell

The Intermittent Adapter can be seen in a special clamp with a Griffith Large Cell containing a glove sample, inverted over the cell. The air line “C” on the right of the cell forces solvent onto the cell. Above it is provision for airlines “D” to pass air (or nitrogen) over the exposed side of the glove sample to more rapidly dry it between exposures. The normal carrier gas lines “A” and “B” are shown at the top of the figure to operate the cell permeation part in the normal way

It would also be desirable to replicate the stresses involved in actions such as lifting a drum or turning a valve. These would be complex and vary greatly over the surface of the glove. We certainly noted

that mechanical failure of gloves sometimes occurred in the web between the fingers as a result of delamination of the polymer and fabric support.

10.7. Mixtures and Modelling

An attempt was made to look at the effect of mixtures on new and used gloves. This work was not completed due to difficulties in retrieving the spectra from a Perkin Elmer 1750 FTIR spectrophotometer and this in turn prevented the development of a model based on our data.

10.7.1. Selection of Mixtures

Mixtures of dissimilar solvents were chosen to ensure that the properties of the mixture was complex and the components of the mixture would interact. The following solvents types were chosen, with the selection of the representative solvent being on the basis of it being commonly used.

- **Ketone.** Acetone. Ketones often lead to severe degradation of the common gloves such as PVC.
- **Aliphatic hydrocarbon.** Hexane
- **Aromatic hydrocarbon.** Toluene

The mixtures prepared were: (the mixtures tested by FTIR are indicated with a *

- *100% hexane
- 20% hexane, 80% toluene
- *40% hexane, 60% toluene
- *50% hexane, 50% toluene
- 60% hexane, 40% toluene
- 80% hexane, 20% toluene
- *100% toluene
- *1:1:1 acetone, hexane, toluene
- 2:1:1 acetone, hexane, toluene

The main solvent processed at the pilot plant was also fractionated and analysed by FTIR. This information has not been used in this report.

10.7.2. FTIR

The entire *GloveTest* rig - cells and solenoids, computer, and nitrogen gas bottles, was taken from the laboratory and connected to a Perkin Elmer 1750 Fourier Transform Infra Red spectrophotometer in the Faculty of Science and Technology. A gas cell was used to receive the output of a single Griffith Large Cell and the output manually recorded and saved on the FTIR computer at about 10 minute intervals up to two hours, though most runs were for about 40 minutes as steady state conditions prevailed. The data was retrieved, but it was found that the spectra were in a format which could not be interpreted on a computer other than that on the FTIR spectrophotometer. The cell volume was large and limited the time resolution of the our measurements, so parallel runs were not possible. The FTIR was set to run at a resolution of 4 cm⁻¹, with 10 scans per sample. The sensitivity was about 1 ppm or 0.25 mg/m³ for toluene, much higher than the estimated 0.0003 mg/m³ for the HNU photoionisation detector.

10.7.3. Modelling

In the absence of useful raw data from the FTIR studies, it was decided not to proceed with the mathematical modelling of the performance of gloves exposed to mixtures. Without the data, the models could not be validated and without validation, the models would be of little use.

10.8. DSC

Differential Scanning Colorimetry was performed on some new and used glove samples. The approach is standard in polymer chemistry to look at structural (phase) changes in polymers. Small (3 mm diameter) samples of glove are inserted in the DSC apparatus and are heated at a constant rate. The amount of energy needed to produce a temperature change (the specific heat of the material) is measured. If there have been changes in the glove structure through swelling, degradation or leaching of plasticiser, then these changes should be evident in the DSC curves. It would be desirable to look at the DSC curves at various points in the permeation mechanism to elucidate the mechanisms involved in the swelling that appears to occur with strong solvent-polymer interactions.

11. RESULTS

The data from this project are complex and a discussion of all aspects of correlations and patterns would make readings of this report too difficult. They have been arranged chronologically to correspond to the three phases of the project - Laboratory Trials, Pilot Trials and Main Trials, with additional results from the Calibrations and Cell Validations. Illustrative examples of what can be calculated with a graphical representation of the data has been attempted to allow lay readers to better follow our approaches.

Pointers are also given to other work - the use of FTIR analysis with mixtures of solvents, DSC analysis and the development of our Intermittent Exposure Cell to give a better understanding of the permeation process and advance the techniques of glove testing so that the data is useful in predicting performance in the workplace.

11.1. Laboratory Trials

The laboratory trials refined the testing methodology and showed us the degree of variability in test results from a glove. This would be useful in calculating what sort of difference we could expect to detect from glove usage. There is a surprising lack of published data on reliability of glove data, and a surprising lack of statistical tools in almost all of the glove literature.

The data set below represents 68 sample measurements of two types of new glove challenged with toluene in the Griffith Large Cells. The measurements are either in seconds or on a scale between 0 and 4095 on the output of the A-D converter. This roughly corresponds to 0 -20 mg/cm²/min. Absolute measurements are not important for comparative studies, but they can be back calculated from the flow rate, glove sample area and the instrument calibration. The gloves were either Ansell single dipped PVC (2A) or Ansell double dipped PVC (2B).

Some statistical tests have been performed on the data for each permeation index to determine the number (n) of measurements that would have to be made to show eight out of ten times (a "power" of 80%) that a real difference can be shown between the measurements with 95% confidence. The statistical methodology is from Kirkwood (p 196, 1988) for determining the number of measurements to demonstrate a real difference between means. The number (n) of measurements has been rounded up to a whole integer as only integer numbers of tests can be made.

The table below shows the statistical summary for the two glove types for the thirteen indices calculated by the *GloveTest* software and shows the number of tests that would be required for each index to show a real difference between the mean values for each glove. Pragmatically, the best choice of index would be one that related to a decision on glove use or selection and required the least number of tests.

	Count 2A	Mean 2A	SDev 2A	Conf 2A	Count 2B	Mean 2B	SDev 2B	Conf 2B	n
Midpoint Time	25	1,459	787	10	43	1,692	657	6	153
Midpoint Value	25	877.7	282	4	43	617	237	2	16
Slope	25	2	1	0	43	1	0	0	5
Intercept	25	-1,426	375	5	43	-917	371	4	9
BreakThrough Time	25	974	827	10	43	958	303	3	25,525
Max Point	25	2,788	335	4	43	1,894	423	4	3
Max Time	25	4,432	1,289	16	43	5,539	1,459	14	25
Top Slope	25	-0	0	0	43	-0	0	0	15
Top Intercept	25	2,934	353	4	43	1,987	446	4	3
Steady State Perm	25	35	11	0	43	16	4	0	3
Lag Time	25	1,922	259	3	43	1,750	261	2	36
Integral 20 min	25	2,217	1,145	14	43	1,641	1,371	13	76
Integral 30 min	25	9,655	3,362	42	43	5,363	2,961	28	9

Table 16 Number of measurements to detect real differences between glove selections

What is important to note is that the number of measurements to show a real difference between runs varies widely between indices. It would be difficult to plan with any certainty the number of measurements that would be needed in the Pilot Trials without deciding beforehand which indices were important. On the advice of our statistical adviser, we aimed at making eight measurements for every factor such as new or used, to be able to investigate SSPR, BT, LT and Integral permeations. This was much larger number than the number of repeats we found in the literature (2 or 3 at the most). Only the degree of automation we had devised for the testing permitted such an approach.

Examination of the table above reveals some useful information. The main index of glove performance in the literature is the Breakthrough Time (BT). As previously discussed, this can be determined using the detection limit of the equipment, or more reproducibly (as some other researchers and this project did) with the time intercept of the permeation curve. The Lag Time (LT) is even less dependent on the analytic sensitivity than the BT and less variation would be expected with repeated tests as a smoothing effect of the *integral* of the permeation curve occurs. This is exactly what is seen in the table above - 36 vs 25,525 measurements are needed to show a true difference. The indications are that the BT is a poor indicator of performance if this index is to be used to select gloves. The LT is better, but the excessive (36) number of measurements needed to decide between the two types of glove is impracticable. In any case, the real question that needs to be answered is the amount of chemical the wearer is exposed to whilst using the glove. The Steady State Permeation Rate (SSPR) and the 20 and 30 minute integrals better answer this. (Time did not permit the retrospective re-calculation of longer integrals, e.g. for 60 and 240 minutes). The SSPR is the most sensitive index, requiring only 3 measurements to differentiate the gloves, but it does not tell us much about the amount of chemical permeating the glove. The variability in time to establish steady state conditions is related more closely to the lag time, and from our data it can be seen that thirty minutes is more preferable than 20 minutes as the number of measurements needed reduced from 76 to 9. Overall, rates rather than times are much more reproducible, but it is information on acceptable protective times that should influence choice. This information is effectively given by the integral measurements such as Int20 and Int30.

The table below shows the percentage difference which may be detected with a power of 80% and with a 95% confidence for a sample size between 1 and 10 for each type of glove. As a percentage, the changes are normalised, and the best indices will be those with the smallest detectable differences. There is no reason to suspect that the figures in this table which compare two types of gloves will not be reflected in other changes between gloves which are new and used. This allows the less sensitive indices to be eliminated when trying to look at differences in performance. Clearly only a single test, or duplicating or replicating a test will provide very poor information about the relative performance of gloves, particularly if the BT is used.

	n	1	2	3	4	5	6	7	8	9	10
Midpoint Time	152	46	32	26	23	20	19	17	16	15	14
Midpoint Value	16	35	24	20	17	15	14	13	12	12	11
Slope	4	30	21	18	15	14	12	11	11	10	10
Intercept	8	32	22	18	16	14	13	12	11	11	10
Breakthrough Time	25524	64	45	37	32	29	26	24	23	21	20
Max Point	3	16	11	9	8	7	7	6	6	5	5
Max Time	24	27	19	16	14	12	11	10	10	9	9
Top Slope	14	60	42	35	30	27	24	23	21	20	19
Top Intercept	3	16	11	9	8	7	7	6	6	5	5
Steady State Permeation Rate	3	33	23	19	16	15	13	12	12	11	10
Lag Time	36	14	10	8	7	6	6	5	5	5	4
Integral 20 minutes	75	65	46	37	32	29	26	25	23	22	20
Integral 30 minutes	9	42	30	24	21	19	17	16	15	14	13

Table 17 Detectable percentage difference for sample size

To imagine what the results would be like for just duplicate measurements, rather than the eight sought in this project, double the length of the confidence intervals on the graphs. When this happens, many of the differences between mean values do not become significant, and no real difference could be reported.

11.2. Pilot Trials

The Laboratory Trials had allowed us to thoroughly test the *GloveTest* Rig on new gloves and the continual process of improving the *GloveTest* software proceeded throughout the project. The Pilot Trials was designed to allow testing of gloves that had been used in the field.

An industry which reprocessed waste solvents was approached for inclusion in these trials. It was here that some of our tacit assumptions outlined in the project proposal were shown to be wrong. We had assumed that the selection of gloves would relate to their chemical resistance and that quality gloves would be chosen and reused. What we found was that cheap PVC gloves were chosen, thrown out daily and the reason for disposal was the dislike of wearing smelly gloves the next day. In fact the reason for wearing gloves was more related to protecting the wearer from smelling of solvent - a social choice, than protection from the toxic effects of the chemicals. The actual amount of contact during the day was limited and very intermittent, so the initial concept of testing at 2, 4 and 8 hours was abandoned, to see initially if there was a difference between new and used gloves. At this stage we also started classifying the test samples from the position on the glove. As we were unable to find anything in the literature on the variability of performance of gloves over their surface, we did not know what to expect. In fact, some of the researchers took unclassified samples “at random” (Leinster, 1986) from the surface of the glove, presumably only limited by the area from which a sample was taken. Our test cells, particularly the Griffith Small Cell could take a “biopsy” sample from any position.

The following table is given to show the code for position, running from fingers to cuff, with half integers representing the back of the glove.

Table 18 Codes for Glove Sample Position



Position	Front	Back
Fingers	1	1.5
Top Palm	2	2.5
Mid Palm	3	3.5
Heel of Palm	4	4.5
Cuff	5	5.5

The rationale for the selection of these position is as follows:

1. **Fingers.** All fingers are taken as equal. Undoubtedly, the little finger usually is usually exposed to less chemicals and stresses than the rest, but further subdivision would be a refinement, not an essential element of this project.
2. **Top Palm.** This area would be particularly exposed during lifting and grasping operations. Blisters usually occur here on those not used to manual work using picks and shovels.
3. **Mid Palm.** This appears to be the site of choice for glove testing by other researchers and in the standards, so it really is the main reference point.
4. **Heel of Palm.** This region could be expected to show some difference as it is less stressed and exposed. Turning valves produces high shear stresses in this area. This was probably the least significant selection.
5. **Cuff.** This area is used when “random sampling” is used for ASTM cell measurements, as this cell requires a large sample area. The cuff should be almost unstressed and unexposed in most operations.

An area that (in retrospect) that requires attention is the **web** between the fingers, particularly the index and middle finger, as this area was observed to fail. sampling with the Griffith Small Cell would be possible, but larger samples would not lie flat due to the curvature of the region.

The Code for the Glove Type is given in the table below (the alternate codes for Glove Type were used in the spreadsheet analysis to allow sorting and graphing. The spreadsheet package (Microsoft Excel v 5.0) was found to have limitations in graphing non numerical parameters:

Table 19 Codes for Glove Type

Glove Type	Project Code
1	MSA PVC (Australian made)
1A or 1.0	MSA PVC Metalguard
1B or 1.5	MSA PVC Solvanguard
2	Ansell
2A or 2.0	Ansell Singe Dipped PVC
2B or 2.5	Ansell Double Dipped PVC
2C	Other (not reported in this report)

11.2.1. Measure what changes?

We were looking for changes with use, but changes in what? Our review of the literature showed that the accepted indices (BT, SSPR) for the performance in gloves all related to testing in the laboratory under quasi reproducible conditions. There was no indication of what changes to expect with gloves in the workplace, though we expected to see the areas of gloves most exposed to mechanical and physical damage to show the most change.

11.2.1.1. Breakthrough Time

The concept of Breakthrough Time was defined in at least three ways -

1. as the instrumental detection limit (not always defined statistically),
2. as a set small permeation rate being reached,
3. as the time intercept of the open loop permeation curve
4. as the time intercept of the integral (closed loop) permeation curve (Lag Time by some)

We rejected the first as being too experiment dependent. The data could not be compared with other published data. The second was rejected as it too, was arbitrary - toxic substances could be a problem at levels lower than a fixed permeation rate. We used the third and eventually developed a software automated, operator independent method of measuring this index. The fourth method was separately measured (again, as part of the software automation)

11.2.1.2. Steady State Permeation Rate.

An “ideal” glove would have a low degree of solvent-polymer interaction so that the permeation process could be considered Fickian and the diffusion rate independent of solvent concentration. Unfortunately, the main type of glove we evaluated - and the one we found in all the solvent based industries we examined was PVC - cheap and easily affected by solvents. This meant that the curves had a hump, rather than a simple sigmoid shape, so that there never was a simple “Steady State Permeation Rate”

11.2.1.3. Position

Our early work also paid no attention to the position that the sample was taken from over the surface of the glove. The testing protocols used by other experimenters and the standard protocols all referred to taking the sample from either the palm or the cuff or both. As we were free from the constraints of taking large samples with our miniature cell, the “Griffith Large Cell” - and even more so with our biopsy cell, the “Griffith Small Cell”, we took samples from areas we expected to be the most exposed and most flexed. When we documented these positions, it soon became evident that position in itself was a factor.

11.2.1.4. Use

The site for the Pilot Trials was a solvent recovery plant which received a mixture of solvents and the table below is extracted from the list of chemicals supplied to the fire brigade.

Table 20 Chemicals used at Pilot Trials site

Solvent	Maximum Use (litres)	Average Use (litres)
Paint Thinners Ifp	253,000	108,000
Fuel Oil	13,000	8,000
Spent Caustic	54,000	36,000
Cresylic Acid	25,000	5,000
White Spirit	4,000	2,000
Kerosene	28,000	7,000
Ind Meths	800	0
Methanol;	200	0
n-Butanal	200	0
Perchloroethylene	800	200
III Trichloroethane	40,000	1,000
Trichloroethylene	200	0
DiAcetone Alcohol	600	0
Toluene	200	0
Xylene	400	200
Methyl Ethyl Ketone	800	200
Acetone	200	0
Butyl Acetate	600	0
Methylene Chloride	600	0
Iso Propanol	200	0
Mineral Turpentine	8,000	2,000
Hydrochloric Acid	1,000	200
Corrosive Liquids N.O.S.	400	0

The main solvent was paint thinners, and this was fractionated and analysed by Fourier Transform Infra Red Spectroscopy. There were difficulties extracting the data from the files as they were in a special format peculiar to Perkin Elmer. With time, this data will be retrieved and used, but not for this project

We expected that appropriate gloves would be selected for the task and that these would be used for a number of days, as good solvent resistant gloves are quite expensive. What we did not expect, was that cheap imported PVC gloves would be in common use, and thrown away like facial tissues. Thus our initial concerns that there may be attempts by employers to extend the wear times while we were looking at the effect of degree of use, were to be unfounded (at least for this project). Exposure was a lot more intermittent than we anticipated - mostly from handling of drums and turning on and off valves. This contrasted with the laboratory trials which allowed the glove sample to be continuously wet with solvent.

A number of questions need to be answered to enable the Pilot Trials to lay the foundation for the main Trials. The first is the number of samples needed to show a real difference between new and used gloves.

11.2.2. Number of samples ?

One of the key figures we planned to extract from the Pilot Trials was an indication of how many samples we would need to make to show differences caused by use of gloves (chemical and mechanical damage) were real. We had to know the degree of variation we could expect with new gloves and between gloves in the same batch, and we looked at a number of used gloves from the same batch as the new gloves to determine whether there was a change. If the change was significant, we wanted to know how many gloves we would have to test to show that this change was real. Statistically, this could be expressed as the Power of the statistical test being at least 90% and the confidence limit 95%.

Unfortunately there was little data in the published literature to give us guidance. The sanctified approach to testing was to do two or perhaps three measurements, and if they were similar, then to take the mean. This approach has been codified in testing protocols (ASTM 1986, Leinster, 1986).

We started this stage of the project with the recommendations of our statistical adviser, based on the Laboratory Trials that eight would be the optimum number.

11.2.3. Selection of permeation indices

We had thirteen indices, which were automatically calculated by the *GloveTest* software from the permeation data for each cell. There was no particular need to cull the data to a smaller set, as disk storage was not a problem. We had already found by chance that Position was a significant factor in determining the permeation characteristics of a glove sample, so we decided to keep the data. In retrospect we should have added more indices to obtain the integral amount of solvent permeating over longer periods - up to one or two hours or whenever the run was truncated.

11.2.4. Difference between gloves

New Ansell PVC gloves were analysed as part of the trials. These were new gloves of the same batch used in the solvent recovery industry. The initial intent was to just see what variation there was between gloves, but as the position the sample was recorded for each sample, it was found that position was of greater importance than inter-glove variation. The following figures and tables show this for new Ansell PVC gloves.

The figure below shows an overall trend of decreasing BT between fingers and cuff. A similar pattern can be seen for the other indices, but would add little to the discussion showing all the figures. This figure shows a plot for a number of gloves and a real difference is seen in the first set of data which represents the BT in samples taken from the front of fingers in three gloves. The data set is reproduced in Appendix G.

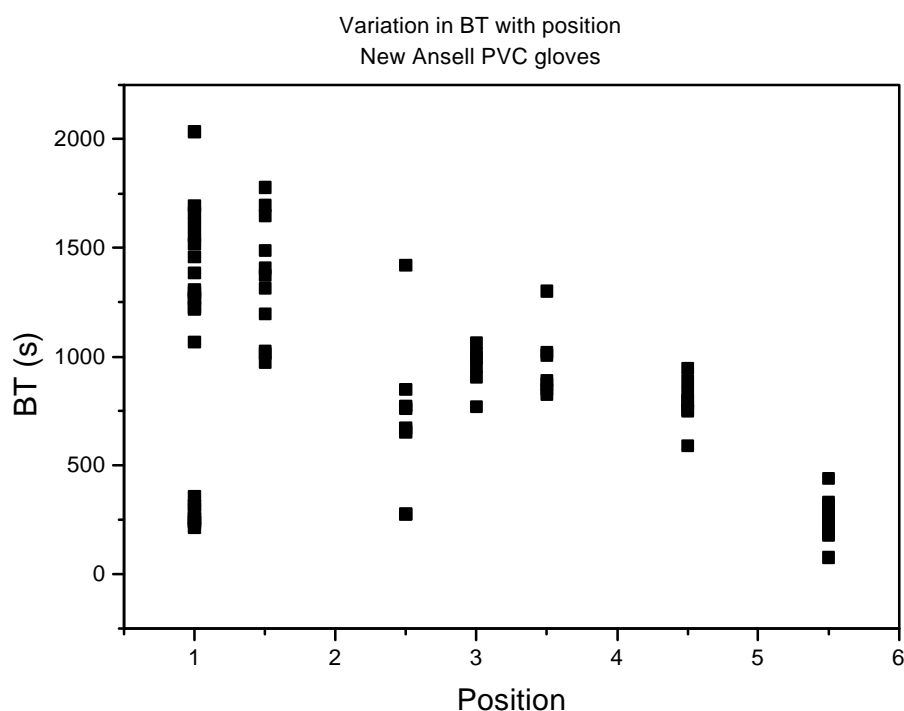


Figure 26 Variation in BT with gloves with Position

Data has been extracted from the same set used to produce the figure above to produce the table below, but only for glove positions where two or more gloves were tested. Thus A, E and F have fronts of fingers in common, F and G have backs of fingers in common and C and D have backs of cuffs in common.

Of particular interest, is the variation between gloves in the same batch compared with the variation over the surface of the gloves. A subset of this data was used, as not all positions on the glove were

replicated between gloves. Three indices BT, LT and SSPR are presented in a tabular form and graphically.

Table 21 Variation with position of indices between gloves

Position	1.0	1.0	1.0	1.5	1.5	5.5	5.5
Run	A	E	F	G	H	C	D
Number	8	8	7	7	4	8	7
UCL	306	1514	1723	1532	1730	320	338
LCL	240	1234	1298	1126	1076	210	199
Average of BT	273	1374	1511	1329	1403	265	268
StdDev of BT	47	202	287	274	334	79	94
UCL	793	2589	2712	2383	2563	1162	965
LCL	650	2418	2522	2066	2029	1076	705
Average of LT	722	2503	2617	2224	2296	1119	835
StdDev of LT	103	123	128	214	272	62	175
UCL	59	21	27	20	20	60	61
LCL	56	17	20	14	10	58	55
Average of SSPR	58	19	23	17	15	59	58
StdDev of SSPR	1.9	2.9	4.4	3.7	5.0	1.4	3.6

Confidence intervals calculated for $\alpha = 0.05$ (95% confidence interval)

Only one run had less than seven data points, and this has significantly increased the indices confidence intervals for that run (see figure below). The Run sequence is kept the same in the three figures below, though only the position is plotted. In Figure 27, only the first sample shows a significant difference when matched for position. The bars on the data points represent the 95% confidence intervals for the mean value plotted. All the other samples show no significant variation between samples if matched for position. Thus, within a batch, it appears that BT varies more over the surface of a glove than between gloves.

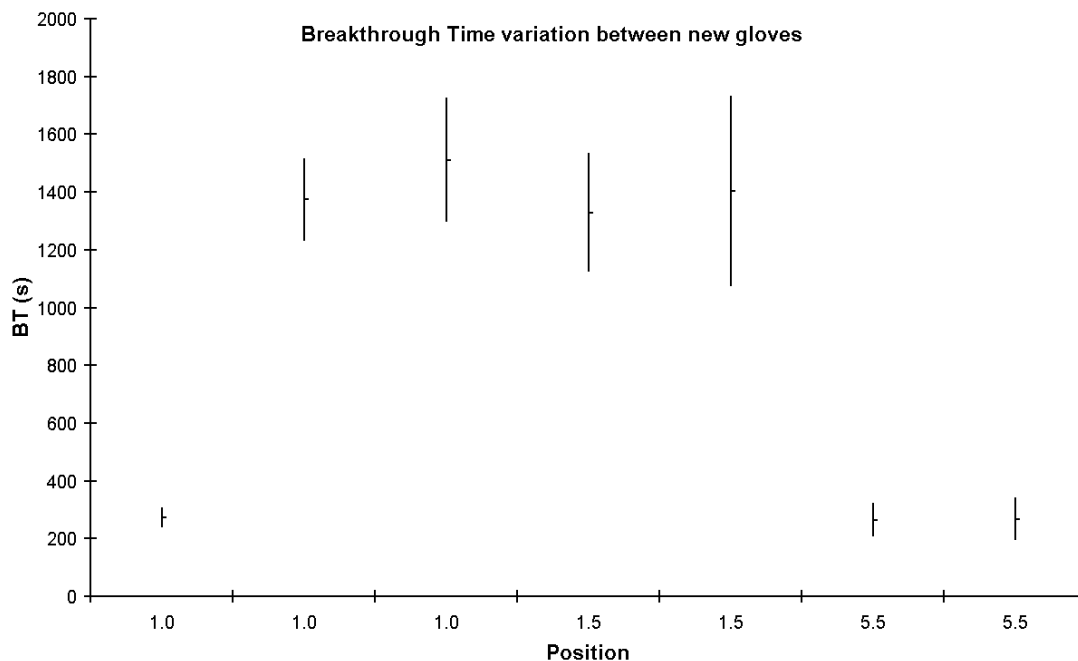


Figure 27 Variation in BT between Ansell PVC gloves

A similar pattern is seen for Lag Times in Figure 29, though there is a significant variation in the LT for the back of the cuff.

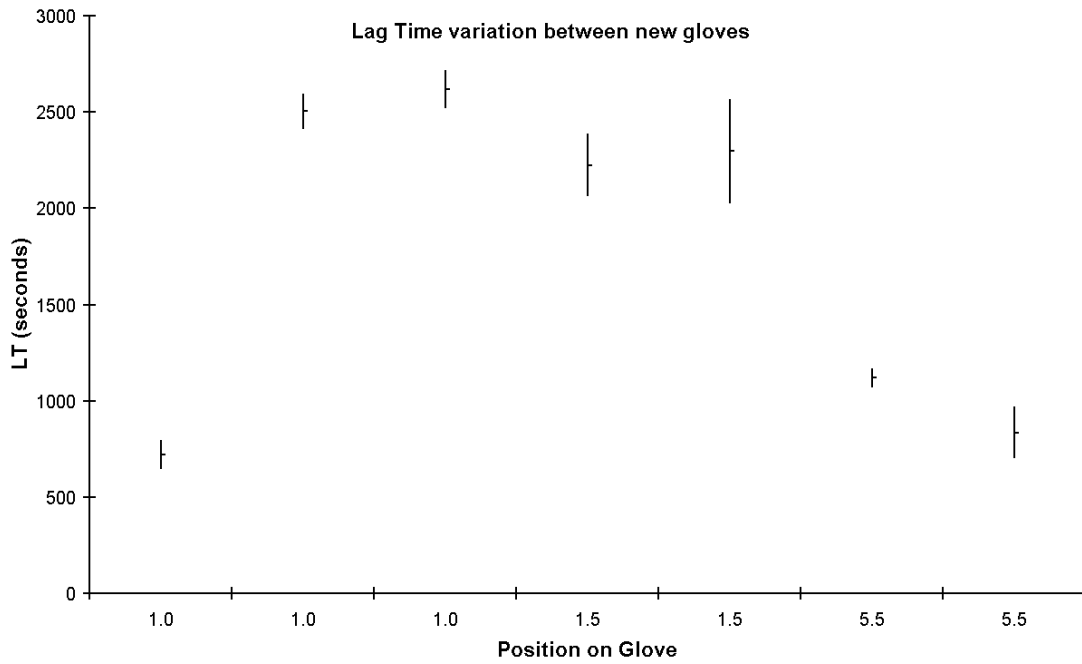


Figure 29 Variation in LT between Ansell PVC gloves

The variations in Steady State Permeation rate between gloves is shown below in “Figure 30 Variation in SSPR between Ansell PVC gloves”. Again the first run shows very different permeation characteristics, and otherwise there is no real difference between gloves, when matched for position.

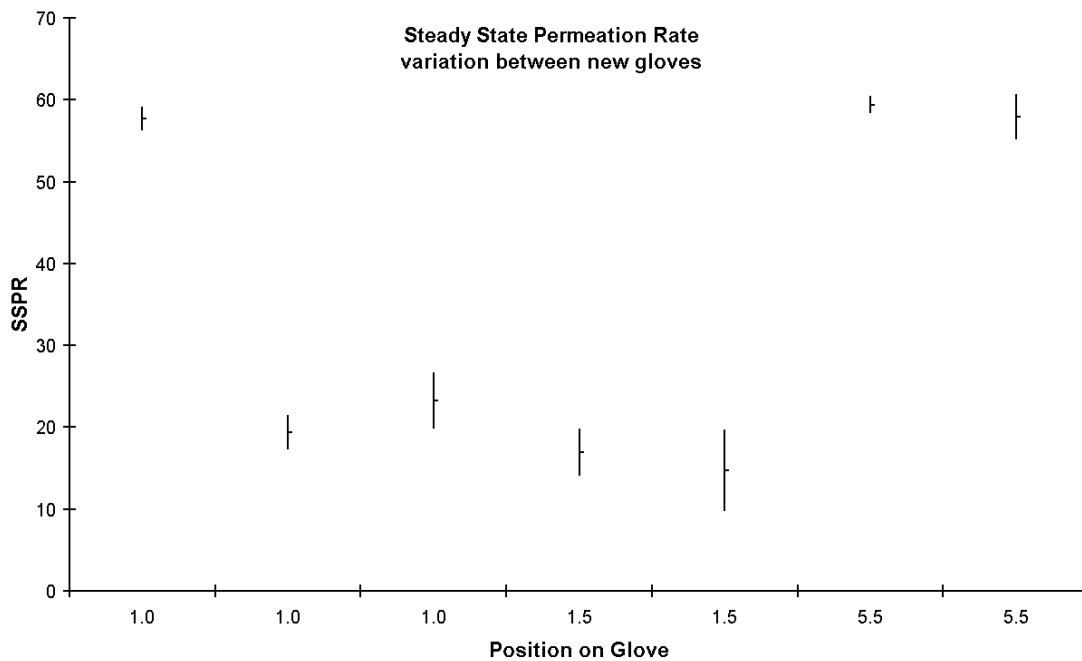


Figure 30 Variation in SSPR between Ansell PVC gloves

The overall impression is that variations are greater over the surface of gloves than between gloves and the permeation varies by about a factor of three. *A test on the palm of one glove, in this instance could underestimate the permeation of the fingers of the glove by a factor of three.* A much more extensive testing program would be needed to establish the typical pattern in the workplace.

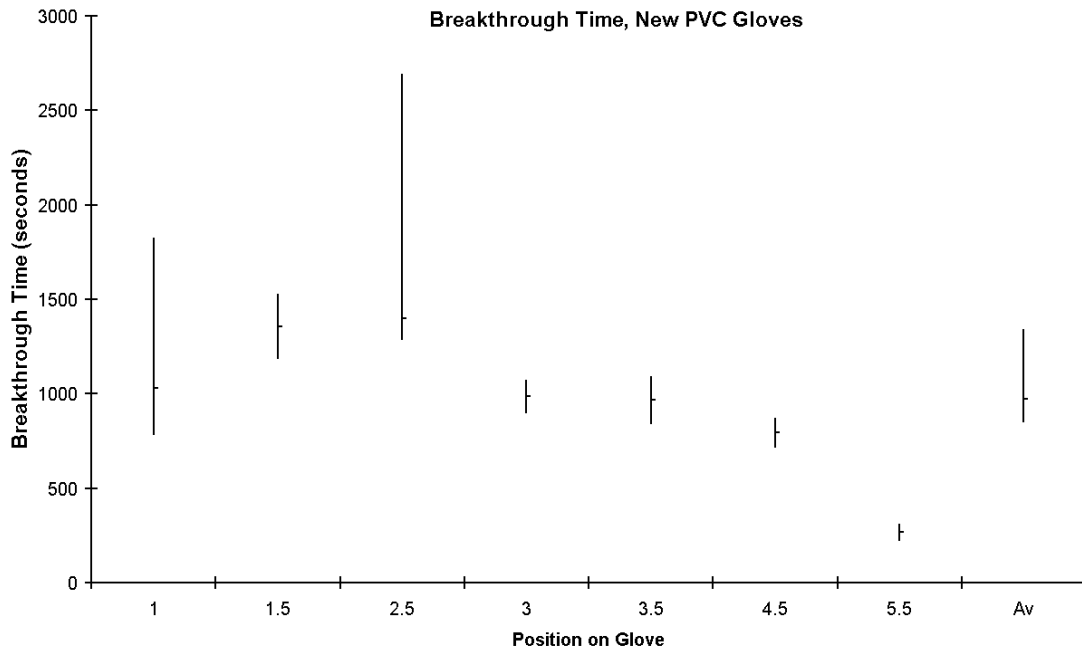


Figure 31 New Ansell PVC gloves: BT and Position

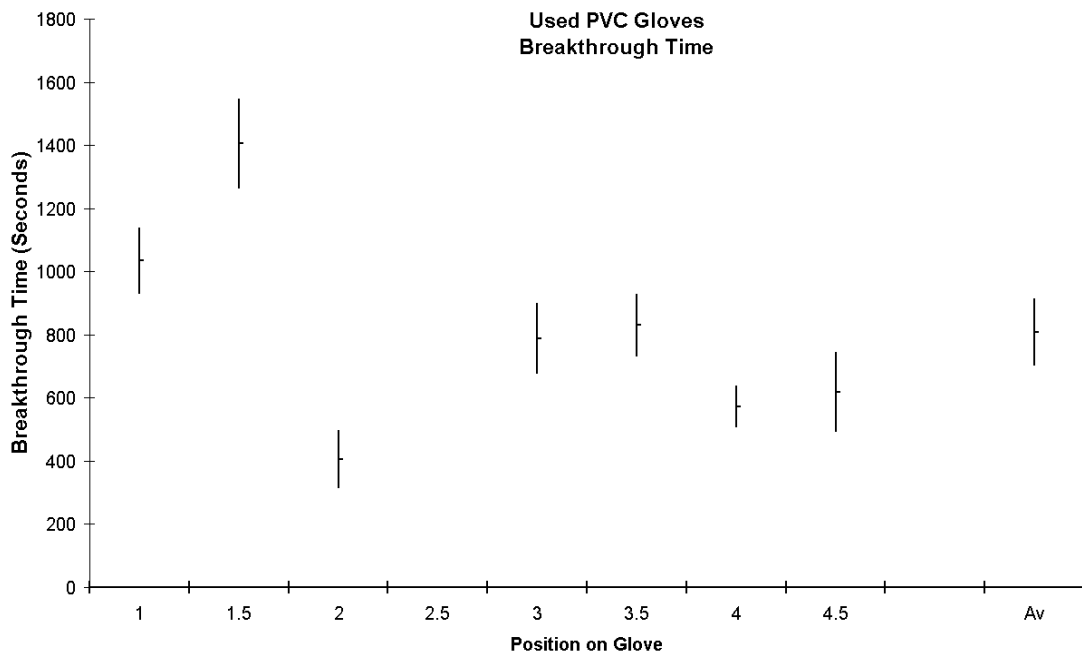


Figure 32 Used Ansell PVC gloves, BT and Position

The data in the two figures above are brought together in “Figure 33 Used and New Ansell PVC gloves, BT compared by position” below. There appears to be a change between new and used gloves, with the change is in the expected direction. The BT has decreased with use, but the change is more dependent on position than use. The positions can be read down the line - the Back of Fingers with the highest BT is essentially unaffected, Front of Fingers is slightly affected, Palm and Back of Palm moderately affected and Heel of Palm most affected.

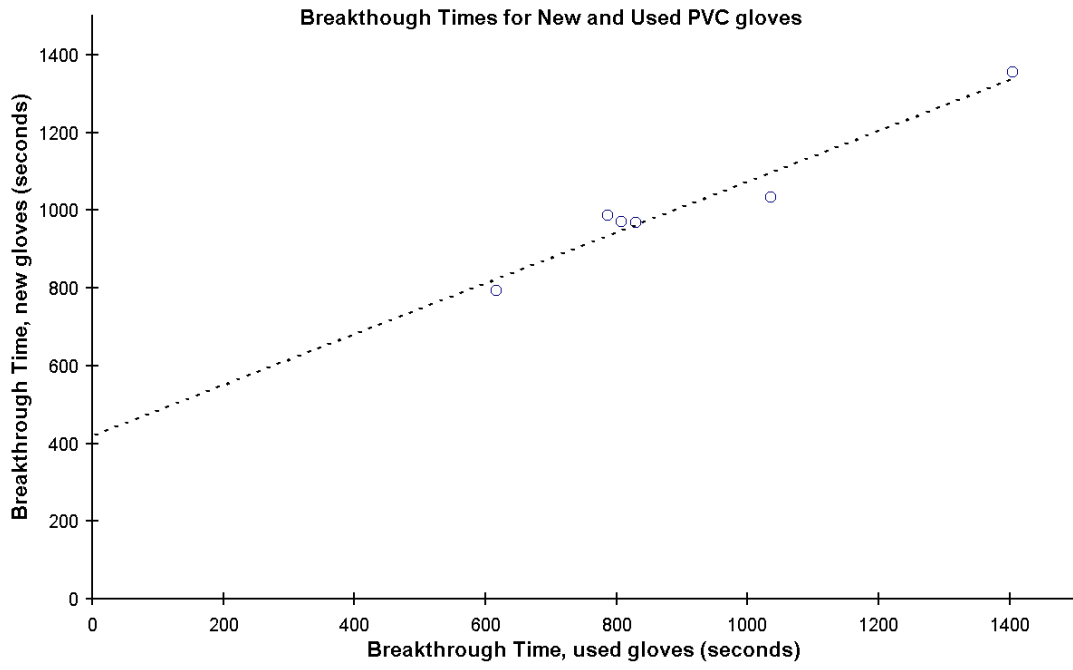


Figure 33 Used and New Ansell PVC gloves, BT compared by position

11.3. Main Trials

11.3.1. Overview of data

A breakdown of the photo-ionisation detector at the most critical time in the project caused several weeks delay and time consuming attempts to source parts and circuit information internationally. This limited the number of measurements on gloves collected from workplaces though the numbers of measurements was considerable as the Position factor had multiplied the number of tests required by a factor of 10 to take account of the front and back of the glove. In two weeks the *GloveTest* Rig, could perform the same number of tests as others using a single channel ASTM cell could in six months. A total of 287 samples were analysed in the Pilot Trials and Main Trials, equating to at least six months work with a single channel test rig, if 3 samples were taken and analysed each day. The samples will be analysed in work continuing from this project, using the current test procedure and others under development

In “Table 22 Number of Measurements” below the number of measurement for each position is not uniform. Where the number of measurements values is less than eight (the number of cells in each run), then this indicates that there were technical problems (such as solenoids sticking or nitrogen running out) during the run and some of the data had to be discarded. Data was not discarded because it did not fit the pattern, but because the data was physically impossible. Two simple rules were used to cull all the bad data (gross outliers) from the final data set.

Rules for discarding data

1. *Samples which exhibited a negative BT were discarded.* A negative BT would mean measuring solvent before the experiment began.
2. *Samples which exhibited a positive intercept of the BT line with the permeation axis were discarded.* As permeation increases with time and then levels off, any real curve should always produce a negative intercept from the rapidly rising part of the curve.

This eliminated 5 samples from the set, leaving 287 sets of data, summarised in the table below.

Table 22 Number of Measurements

Glove Type		Position of Sample on Glove										
		1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	Total
1A	New	12	15	0	0	8	0	0	0	16	27	78
1B	Used	12	0	3	4	4	4	2	3	8	7	47
2B	New	23	11	0	8	6	7	0	8	0	15	78
2B	Used	15	8	8	0	8	8	23	14	0	0	84
Total		62	34	11	12	26	19	25	25	24	49	287

It was not possible to look at all variables -

- glove type or brand of glove. (five workplaces but 7 glove types)
- position of glove, including back and front, (10 positions)
- glove usage - new or used (2)

and determine the contribution of each factor in the performance of the glove. Simple arithmetic shows that $8 \times 7 \times 10 \times 2 = 1120$ samples are needed to characterise the gloves, assuming only one pair to characterise new and used. To put this in perspective a huge number of readings would be taken by the *GloveTest* rig, as each measurements is taken in triplicate and averaged and a run takes 40 to 100 of these averages, a total of up to 336,000 readings, an impossibly boring task to do manually.

Table 23 Industries participating in project

	New Glove Trials	Used Glove Trials	Comment
Solvent recovery	78 PVC	84 PVC	Used for Pilot Trials
Government Dept	not applicable	47 PVC	Given a pair of failed gloves.
Petrochemical 1	samples collected	78 PVC	Most analysis completed. PVC and vinyl gloves
Petrochemical 2	samples collected	samples collected	Observations of use. PVC and vinyl gloves
Paint industry	samples collected	samples collected	Observations of use

An alternative, as there was insufficient time to complete the analysis program - the cell validation and calibrations had also to be completed, was to extract sufficient information from what we had done to make valid suppositions. The shaded boxes in “Table 22 Number of Measurements” allow the examination of trends to answer the questions below, relating to glove use and sample position on the glove.

11.3.2. Questions asked

Questions that were asked include:

1. Was there any trend with position along the **back** of a **new** glove from fingers to cuff in the performance of the glove?
2. Was there any trend with position along the **front** of a **new** glove from fingers to cuff in the performance of the glove?
3. Was there any trend with position along the **front** of a **used** glove from fingers to cuff in the performance of the glove?
4. Did **Use** make a difference and does this vary between fingers and palm?

Interestingly, if we had managed to make an equal number of measurements in each box in “Table 22 Number of Measurements”, then the average would be seven, and highly significant correlations between the above variables and the glove performance indices would have been possible.

11.3.3. Effect of Position

A total of 78 trials challenging the Australian made new (Code 1A) MSA Metalguard PVC gloves showed a much greater uniformity of performance not over the entire glove. This probably relates to greater quality in manufacture than the cheaper imported gloves. The 95 percent confidence intervals for the trials at different positions are shown below. The data for the tables is in Appendix H.

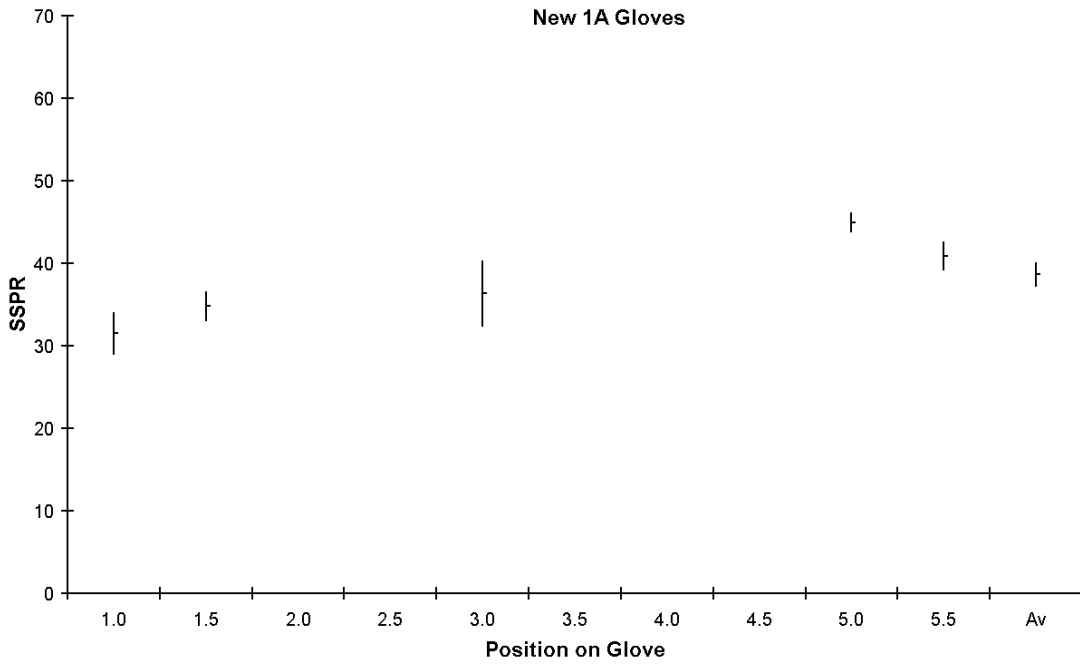


Figure 34 SSPR: New MSA Metalguard gloves

The next set of gloves was given to us by a government agency which was having problems with their gloves and approached us. We were able to suggest to them a more suitable alternative and chose to analyse the used gloves they gave us. We did not visit the workplace and no ethical clearance or workplace agreement was obtained for their use as the inclusion of this pair of gloves was so remote from the intent of our ethical agreements to prevent unauthorised human experimentation.

In “Figure 35 SSPR: Used MSA Solvanguard gloves”, the effect of position on the Steady State Permeation Rate through used (Code 1B) MSA Solvanguard PVC gloves is seen. The gloves were brittle from use with chloroform which had leached much of the plasticiser from the glove. The lines show the 95% confidence intervals for the means of the measurements.).

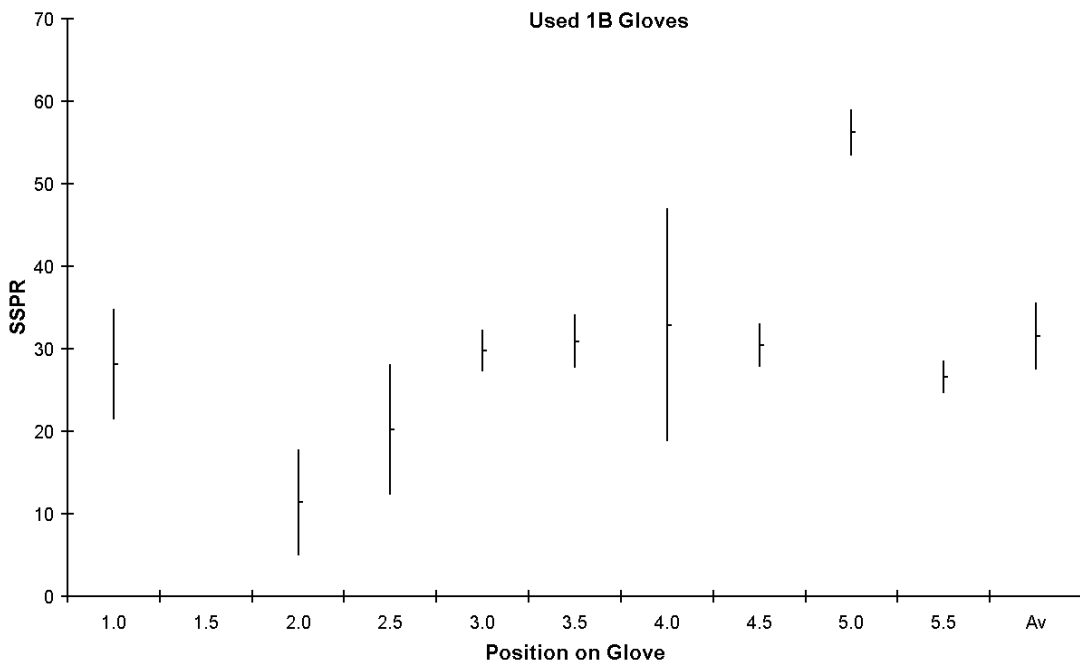


Figure 35 SSPR: Used MSA Solvanguard gloves

On the front of the glove, signified by integer values, a significant difference is evident between the top palm (2) and mid palm (3) and cuff (5), with increasing permeability either attributable to changes in glove thickness or damage by the chloroform. As the only significant difference between front and back of the glove (2 to 2.5, 3 to 3.5 etc.) is on the cuff, and as this region was least exposed (still flexible) it is likely that variations in thickness was the major factor, not use. The stiffness caused by the leaching of polymer would make the glove more prone to mechanical damage, though on re-exposure to solvents, the solvent would perform some of the task of the plasticiser and soften the glove (and expose the user to solvent)

The pattern of steady state permeation is very different for the new and used (Code 2B) Ansell Double Dipped PVC gloves in the figures below. There is a significant differences along the back of the glove at each point between fingers and cuff. The same pattern does not exist on the front of the glove except between cuff and the rest of the glove. There are significant differences between the front and back of the glove in all positions where pairs of measurements were made.

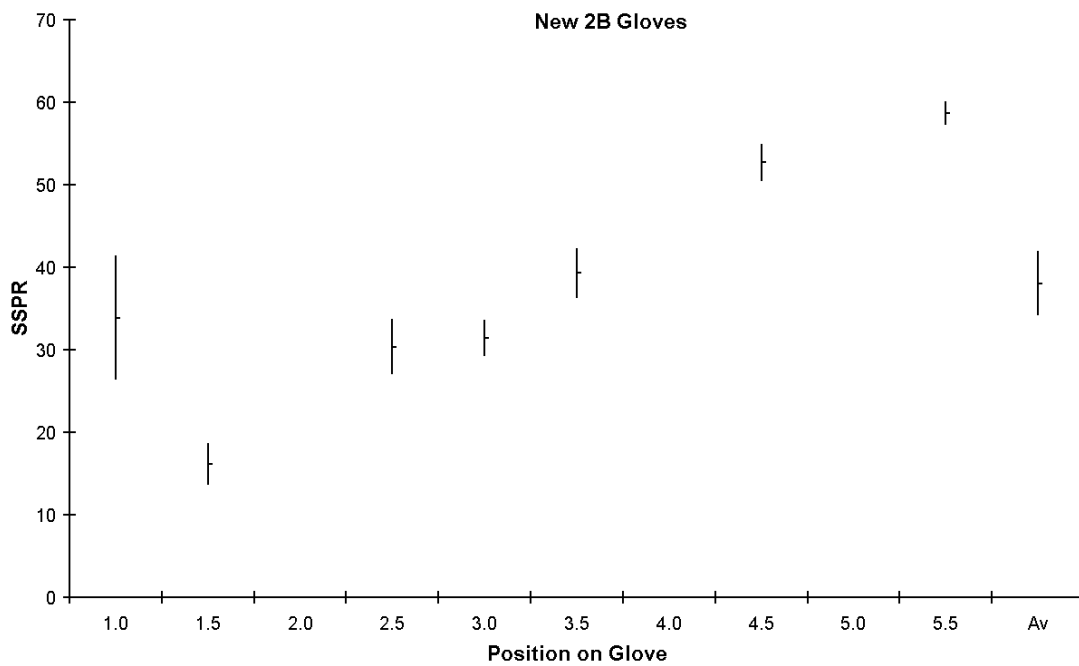


Figure 36 SSPR: New Double Dipped PVC gloves

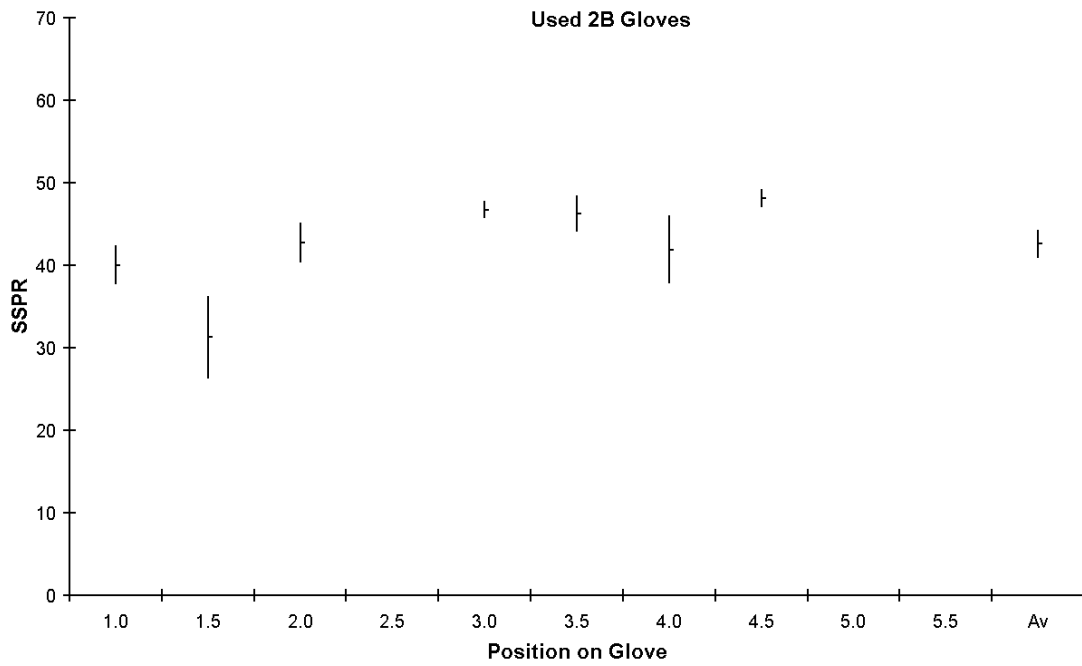


Figure 37 Used MSA Solvguard gloves

All the data was analysed using the GLIM package from SAS to determine whether there were any correlations between our measurements. The table below is extracted from the same data set shown in Appendix F “Main Trials Data” showing a set of data to answer the questions on page 61

The codes used for the table headings were

Table 24 Codes for correlation tables

Code	Pos	Type	New
1	1	1	1
2	1	2.5	1
3	3	1	1
4	3	2.5	1
5	5	1	1
6	1.5	1	1
7	1.5	2.5	1
8	2.5	2.5	1
9	3.5	2.5	1
10	4.5	2.5	1
11	5.5	1	1
12	5.5	2.5	1
13	1	1.5	2
14	1	2.5	2
15	2	1.5	2
16	2	2.5	2
17	3	1.5	2
18	3	2.5	2
19	4	1.5	2
20	4	2.5	2
21	5	1.5	2
22	1.5	2.5	2
23	2.5	1.5	2
24	3.5	1.5	2
25	3.5	2.5	2
26	4.5	1.5	2
27	4.5	2.5	2
28	5.5	1.5	2

Only a subset of the codes was needed to answer the questions as only some of the permutations of Use, Position and Glove Type were investigated. The codes for Position, Type and New are numerical - New = 1, Used =2, Position 1-5.5 for position from fingers to cuff, front and back (#.5); an Glove Type per Table 25.

Table 25 Codes for Glove Position and Glove Type



Glove Type	Project Code
1	MSA PVC (Australian made)
1A or 1.0	MSA PVC Metalguard AMPOL
1B or 1.5	MSA PVC Solvanguard
2	Ansell
2A or 2.0	Ansell Singe Dipped PVC
2B or 2.5	Ansell Double Dipped PVC
2C	Other (not reported in this report)

The tables in Appendix F show the difference between measurements of indices taking into account Use, Position and Glove Type plus the probabilities associated with these differences being real. The degree of significance was accepted was $p = 0.01$ or 99% - numbers in the table less than this are considered significant.

Example: Variation of permeation with position

“Figure 36 SSPR: New Double Dipped PVC gloves” above shows the mean SSPR’s and their associated confidence intervals for New Double Dipped gloves at different positions along a glove. The data for the SSPR along the back of the glove (position 1.5, 2.5, 3.5, 4.5, 5.5) appears to show a trend of increasing permeation. Are the differences significant?

To see if the SSPR was significantly different between the

- data points (position 1.5, 2.5, 3.5, 4.5, 5.5 - see “gloves” above
- for new Ansell Double Dipped PVC gloves - see “Table 25 Codes for Glove Position and Glove Type” above

The codes from “Table 24 Codes for correlation tables”, give us codes 7, 8, 9, 10 and 12 with the associated probabilities from “Table 27 Selected Correlation Probabilities

Index	Code	3	5	7	8	9	10	12	14	16	18	20
BT	1	0.984	0.0001	0.6712	0.0001	0.002	0.0001	0.0001	0.0014	0.0001	0.0001	0.0001
INT20	1	0.8114	0.0001	0.7868	0.1119	0.7964	0.3059	0.0001	0.4421	0.0059	0.0646	0.0001
INT30	1	0.7989	0.0001	0.5816	0.0436	0.7702	0.0017	0.0001	0.1241	0.001	0.0003	0.0001
LT	1	0.2228	0.0001	0.8488	0.0003	0.7031	0.0001	0.0001	0.0319	0.009	0.0001	0.0001
SSPERM	1	0.1484	0.0001	0.0001	0.7408	0.0263	0.0001	0.0001	0.0019	0.0009	0.0001	0.0001
INT20	3		0.0003	0.9931	0.0953	0.6546	0.2494	0.0001	0.3532	0.0064	0.057	0.0001
INT30	3		0.0001	0.4562	0.1067	0.9651	0.0083	0.0001	0.2728	0.0056	0.0019	0.0001
LT	3		0.0001	0.3045	0.0291	0.4679	0.0066	0.0001	0.5265	0.1998	0.0047	0.0001
SSPERM	3		0.0073	0.0001	0.1053	0.4393	0.0001	0.0001	0.2075	0.0833	0.0052	0.0671
INT20	7	0.9931	0.0001		0.0714	0.6261	0.2121	0.0001	0.3013	0.0033	0.0398	0.0001
INT30	7	0.4562	0.0001		0.0135	0.4456	0.0004	0.0001	0.038	0.0002	0.0001	0.0001
LT	7	0.3045	0.0001		0.0008	0.8333	0.0001	0.0001	0.058	0.0166	0.0001	0.0001
SSPERM	7	0.0001	0.0001		0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
INT20	8	0.0953	0.0836	0.0714		0.2433	0.6038	0.0001	0.327	0.2823	0.8122	0.0493
INT30	8	0.1067	0.0009	0.0135		0.1297	0.2983	0.0001	0.4541	0.2414	0.1312	0.0032
LT	8	0.0291	0.0026	0.0008		0.0048	0.5883	0.0001	0.0623	0.3642	0.5121	0.0087
SSPERM	8	0.1053	0.0001	0.0001		0.0198	0.0001	0.0001	0.002	0.0009	0.0001	0.0002
INT20	9	0.6546	0.003	0.6261	0.2433		0.5051	0.0001	0.702	0.028	0.1629	0.0012
INT30	9	0.9651	0.0001	0.4456	0.1297		0.0121	0.0001	0.3175	0.0084	0.0031	0.0001
LT	9	0.4679	0.0001	0.8333	0.0048		0.0009	0.0001	0.1543	0.05	0.0006	0.0001
SSPERM	9	0.4393	0.0901	0.0001	0.0198		0.0005	0.0001	0.7396	0.3663	0.0524	0.413
INT20	10	0.2494	0.0202	0.2121	0.6038	0.5051		0.0001	0.6979	0.1115	0.4494	0.0096
INT30	10	0.0083	0.0312	0.0004	0.2983	0.0121		0.0001	0.0535	0.8951	0.6372	0.0901
LT	10	0.0066	0.0165	0.0001	0.5883	0.0009		0.0005	0.0134	0.148	0.9089	0.0483
SSPERM	10	0.0001	0.0161	0.0001	0.0001	0.0005		0.0628	0.0002	0.0073	0.1059	0.0004
INT20	14	0.3532	0.0011	0.3013	0.327	0.702	0.6979	0.0001		0.0278	0.2111	0.0002
INT30	14	0.2728	0.0001	0.038	0.4541	0.3175	0.0535	0.0001		0.0375	0.0138	0.0001
LT	14	0.5265	0.0001	0.058	0.0623	0.1543	0.0134	0.0001		0.4052	0.0093	0.0001
SSPERM	14	0.2075	0.0863	0.0001	0.002	0.7396	0.0002	0.0001		0.4709	0.0516	0.544
INT20	16	0.0064	0.6227	0.0033	0.2823	0.028	0.1115	0.0001	0.0278		0.402	0.5077
INT30	16	0.0056	0.0451	0.0002	0.2414	0.0084	0.8951	0.0001	0.0375		0.7341	0.1247
LT	16	0.1998	0.0001	0.0166	0.3642	0.05	0.148	0.0001	0.4052		0.1187	0.0002
SSPERM	16	0.0833	0.4853	0.0001	0.0009	0.3663	0.0073	0.0001	0.4709		0.281	0.7806
INT20	18	0.057	0.145	0.0398	0.8122	0.1629	0.4494	0.0001	0.2111	0.402		0.093
INT30	18	0.0019	0.1063	0.0001	0.1312	0.0031	0.6372	0.0001	0.0138	0.7341		0.2611
LT	18	0.0047	0.0233	0.0001	0.5121	0.0006	0.9089	0.0008	0.0093	0.1187		0.0663
SSPERM	18	0.0052	0.5838	0.0001	0.0001	0.0524	0.1059	0.0002	0.0516	0.281		0.112

”, extracted from this table and tabulated below with the longer descriptions and the codes:

Table 26 Probabilities SSPR are different - back of a new double dipped PVC glove

SSPR		Top Palm	Mid palm	Heal of Palm	Cuff
	Code	8	9	10	12
Fingers	7	0.0001	0.0001	0.0001	0.0001
Top Palm	8		0.0198	0.0001	0.0001
Mid Palm	9			0.0005	0.0001
Heal of Palm	10				0.0628

Note that the table above does not have all the positions along both axes nor fill all the squares, as the information would be redundant - comparing Fingers with Cuff is the same as Cuff with Fingers.

Table 27 Selected Correlation Probabilities

Index	Code	3	5	7	8	9	10	12	14	16	18	20
BT	1	0.984	0.0001	0.6712	0.0001	0.002	0.0001	0.0001	0.0014	0.0001	0.0001	0.0001
INT20	1	0.8114	0.0001	0.7868	0.1119	0.7964	0.3059	0.0001	0.4421	0.0059	0.0646	0.0001
INT30	1	0.7989	0.0001	0.5816	0.0436	0.7702	0.0017	0.0001	0.1241	0.001	0.0003	0.0001
LT	1	0.2228	0.0001	0.8488	0.0003	0.7031	0.0001	0.0001	0.0319	0.009	0.0001	0.0001
SSPERM	1	0.1484	0.0001	0.0001	0.7408	0.0263	0.0001	0.0001	0.0019	0.0009	0.0001	0.0001
INT20	3		0.0003	0.9931	0.0953	0.6546	0.2494	0.0001	0.3532	0.0064	0.057	0.0001
INT30	3		0.0001	0.4562	0.1067	0.9651	0.0083	0.0001	0.2728	0.0056	0.0019	0.0001
LT	3		0.0001	0.3045	0.0291	0.4679	0.0066	0.0001	0.5265	0.1998	0.0047	0.0001
SSPERM	3		0.0073	0.0001	0.1053	0.4393	0.0001	0.0001	0.2075	0.0833	0.0052	0.0671
INT20	7	0.9931	0.0001		0.0714	0.6261	0.2121	0.0001	0.3013	0.0033	0.0398	0.0001
INT30	7	0.4562	0.0001		0.0135	0.4456	0.0004	0.0001	0.038	0.0002	0.0001	0.0001
LT	7	0.3045	0.0001		0.0008	0.8333	0.0001	0.0001	0.058	0.0166	0.0001	0.0001
SSPERM	7	0.0001	0.0001		0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
INT20	8	0.0953	0.0836	0.0714		0.2433	0.6038	0.0001	0.327	0.2823	0.8122	0.0493
INT30	8	0.1067	0.0009	0.0135		0.1297	0.2983	0.0001	0.4541	0.2414	0.1312	0.0032
LT	8	0.0291	0.0026	0.0008		0.0048	0.5883	0.0001	0.0623	0.3642	0.5121	0.0087
SSPERM	8	0.1053	0.0001	0.0001		0.0198	0.0001	0.0001	0.002	0.0009	0.0001	0.0002
INT20	9	0.6546	0.003	0.6261	0.2433		0.5051	0.0001	0.702	0.028	0.1629	0.0012
INT30	9	0.9651	0.0001	0.4456	0.1297		0.0121	0.0001	0.3175	0.0084	0.0031	0.0001
LT	9	0.4679	0.0001	0.8333	0.0048		0.0009	0.0001	0.1543	0.05	0.0006	0.0001
SSPERM	9	0.4393	0.0901	0.0001	0.0198		0.0005	0.0001	0.7396	0.3663	0.0524	0.413
INT20	10	0.2494	0.0202	0.2121	0.6038	0.5051		0.0001	0.6979	0.1115	0.4494	0.0096
INT30	10	0.0083	0.0312	0.0004	0.2983	0.0121		0.0001	0.0535	0.8951	0.6372	0.0901
LT	10	0.0066	0.0165	0.0001	0.5883	0.0009		0.0005	0.0134	0.148	0.9089	0.0483
SSPERM	10	0.0001	0.0161	0.0001	0.0001	0.0005		0.0628	0.0002	0.0073	0.1059	0.0004
INT20	14	0.3532	0.0011	0.3013	0.327	0.702	0.6979	0.0001		0.0278	0.2111	0.0002
INT30	14	0.2728	0.0001	0.038	0.4541	0.3175	0.0535	0.0001		0.0375	0.0138	0.0001
LT	14	0.5265	0.0001	0.058	0.0623	0.1543	0.0134	0.0001		0.4052	0.0093	0.0001
SSPERM	14	0.2075	0.0863	0.0001	0.002	0.7396	0.0002	0.0001		0.4709	0.0516	0.544
INT20	16	0.0064	0.6227	0.0033	0.2823	0.028	0.1115	0.0001	0.0278		0.402	0.5077
INT30	16	0.0056	0.0451	0.0002	0.2414	0.0084	0.8951	0.0001	0.0375		0.7341	0.1247
LT	16	0.1998	0.0001	0.0166	0.3642	0.05	0.148	0.0001	0.4052		0.1187	0.0002
SSPERM	16	0.0833	0.4853	0.0001	0.0009	0.3663	0.0073	0.0001	0.4709		0.281	0.7806
INT20	18	0.057	0.145	0.0398	0.8122	0.1629	0.4494	0.0001	0.2111	0.402		0.093
INT30	18	0.0019	0.1063	0.0001	0.1312	0.0031	0.6372	0.0001	0.0138	0.7341		0.2611
LT	18	0.0047	0.0233	0.0001	0.5121	0.0006	0.9089	0.0008	0.0093	0.1187		0.0663
SSPERM	18	0.0052	0.5838	0.0001	0.0001	0.0524	0.1059	0.0002	0.0516	0.281		0.112

There is a real trend (p 0.0001 or 99.99% for most points) not just a random variation, as can be seen in “Figure 36 SSPR: New Double Dipped PVC gloves”. Not all of the points are significantly different from all the others. Heel of Palm and Cuff (p 0.0628), Mid Palm and Heel of Palm (0.0198, 98%)..

If the glove is to protect against heavy soiling, something like three times the exposure will occur through the cuff as the fingers. As testing is generally done on the cuff and palm areas as the ASTM cell requires a large sample area, the testing from selection of sample position is conservative. If this variation is due to glove thickness alone, then it may be that the tests on the cuffs of cheap gloves are more conservative than the tests on quality gloves as a greater variation in thickness may be expected on cheap gloves. The degree of variation between gloves in different batches is unknown, as care was taken to select gloves from what we thought was the same batch (the same box).

The same trend may be apparent with the new (Australian) MSA Metalguard gloves in Figure 34 SSPR: New MSA Metalguard gloves, but the data set is not as complete. The slope of the line is not as much, indicating a weaker trend. This may relate to quality of manufacture.

11.3.4. Effect of position and use

A similar approach will be applied to the effects of use on glove performance, again using correlation probabilities from “Table 27 Selected Correlation Probabilities

Index	Code	3	5	7	8	9	10	12	14	16	18	20
BT	1	0.984	0.0001	0.6712	0.0001	0.002	0.0001	0.0001	0.0014	0.0001	0.0001	0.0001
INT20	1	0.8114	0.0001	0.7868	0.1119	0.7964	0.3059	0.0001	0.4421	0.0059	0.0646	0.0001
INT30	1	0.7989	0.0001	0.5816	0.0436	0.7702	0.0017	0.0001	0.1241	0.001	0.0003	0.0001
LT	1	0.2228	0.0001	0.8488	0.0003	0.7031	0.0001	0.0001	0.0319	0.009	0.0001	0.0001
SSPERM	1	0.1484	0.0001	0.0001	0.7408	0.0263	0.0001	0.0001	0.0019	0.0009	0.0001	0.0001
INT20	3		0.0003	0.9931	0.0953	0.6546	0.2494	0.0001	0.3532	0.0064	0.057	0.0001
INT30	3		0.0001	0.4562	0.1067	0.9651	0.0083	0.0001	0.2728	0.0056	0.0019	0.0001
LT	3		0.0001	0.3045	0.0291	0.4679	0.0066	0.0001	0.5265	0.1998	0.0047	0.0001
SSPERM	3		0.0073	0.0001	0.1053	0.4393	0.0001	0.0001	0.2075	0.0833	0.0052	0.0671
INT20	7	0.9931	0.0001		0.0714	0.6261	0.2121	0.0001	0.3013	0.0033	0.0398	0.0001
INT30	7	0.4562	0.0001		0.0135	0.4456	0.0004	0.0001	0.038	0.0002	0.0001	0.0001
LT	7	0.3045	0.0001		0.0008	0.8333	0.0001	0.0001	0.058	0.0166	0.0001	0.0001
SSPERM	7	0.0001	0.0001		0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
INT20	8	0.0953	0.0836	0.0714		0.2433	0.6038	0.0001	0.327	0.2823	0.8122	0.0493
INT30	8	0.1067	0.0009	0.0135		0.1297	0.2983	0.0001	0.4541	0.2414	0.1312	0.0032
LT	8	0.0291	0.0026	0.0008		0.0048	0.5883	0.0001	0.0623	0.3642	0.5121	0.0087
SSPERM	8	0.1053	0.0001	0.0001		0.0198	0.0001	0.0001	0.002	0.0009	0.0001	0.0002
INT20	9	0.6546	0.003	0.6261	0.2433		0.5051	0.0001	0.702	0.028	0.1629	0.0012
INT30	9	0.9651	0.0001	0.4456	0.1297		0.0121	0.0001	0.3175	0.0084	0.0031	0.0001
LT	9	0.4679	0.0001	0.8333	0.0048		0.0009	0.0001	0.1543	0.05	0.0006	0.0001
SSPERM	9	0.4393	0.0901	0.0001	0.0198		0.0005	0.0001	0.7396	0.3663	0.0524	0.413
INT20	10	0.2494	0.0202	0.2121	0.6038	0.5051		0.0001	0.6979	0.1115	0.4494	0.0096
INT30	10	0.0083	0.0312	0.0004	0.2983	0.0121		0.0001	0.0535	0.8951	0.6372	0.0901
LT	10	0.0066	0.0165	0.0001	0.5883	0.0009		0.0005	0.0134	0.148	0.9089	0.0483
SSPERM	10	0.0001	0.0161	0.0001	0.0001	0.0005		0.0628	0.0002	0.0073	0.1059	0.0004
INT20	14	0.3532	0.0011	0.3013	0.327	0.702	0.6979	0.0001		0.0278	0.2111	0.0002
INT30	14	0.2728	0.0001	0.038	0.4541	0.3175	0.0535	0.0001		0.0375	0.0138	0.0001
LT	14	0.5265	0.0001	0.058	0.0623	0.1543	0.0134	0.0001		0.4052	0.0093	0.0001
SSPERM	14	0.2075	0.0863	0.0001	0.002	0.7396	0.0002	0.0001		0.4709	0.0516	0.544
INT20	16	0.0064	0.6227	0.0033	0.2823	0.028	0.1115	0.0001	0.0278		0.402	0.5077
INT30	16	0.0056	0.0451	0.0002	0.2414	0.0084	0.8951	0.0001	0.0375		0.7341	0.1247
LT	16	0.1998	0.0001	0.0166	0.3642	0.05	0.148	0.0001	0.4052		0.1187	0.0002
SSPERM	16	0.0833	0.4853	0.0001	0.0009	0.3663	0.0073	0.0001	0.4709		0.281	0.7806
INT20	18	0.057	0.145	0.0398	0.8122	0.1629	0.4494	0.0001	0.2111	0.402		0.093
INT30	18	0.0019	0.1063	0.0001	0.1312	0.0031	0.6372	0.0001	0.0138	0.7341		0.2611
LT	18	0.0047	0.0233	0.0001	0.5121	0.0006	0.9089	0.0008	0.0093	0.1187		0.0663
SSPERM	18	0.0052	0.5838	0.0001	0.0001	0.0524	0.1059	0.0002	0.0516	0.281		0.112

”, and showing the results in a graphical form.

The effects of Position and Use should not be considered separately as use of a glove will affect some parts of a glove more than others. It would be expected that the fingers would be more affected than the cuff in all but the most exceptional cases. The effect of use should be able to be considered in terms of mechanical effects - stretching and shearing forces - such as those tending to tear a glove when turning a tap handle; and chemical effects from contact with a solvent. Both are difficult to model, but this should not prevent attempts to develop tests which relate to workplace use. The importance of that Position -not specifically examined by other researchers and in glove testing standards, was so important, was not realised until we started categorising position during the Pilot Trials. The figures below indicate the relative importance of position to use.

The gloves are thought to come from the same manufacturing batch as they came from the same box at the solvent recovery plant. The used gloves came from a pile of gloves from the same box which had been used for one day and discarded. The table below shows the BT for new and used gloves matched for Position - fingers to cuff for the test sample. If there was no difference in BT with use, then a best fit line through the data would be expected to pass through the origin of the plot. There is an effect, which correlates with position. The data here is the same data used to plot "Figure 38 BT - New and Used Ansell PVC gloves" and "Figure 41 New and Used LT, matched for position" and appears in the "Table 28 Effect of Position and Use: Ansell PVC gloves" below. The data set was incomplete - there were ten possible positions, but matched data was only available for six.

"Table 28 Effect of Position and Use" below shows the main permeation indices - BT, LT, SSPR and the two integrals Int20 and Int30. The statistics calculated are the number of measurements (Count), The Upper Confidence Limit (UCL) and Lower Confidence Limit (LCL) of the mean (\bar{A}_v) of each index. This is done for each of the glove positions. All the position data has also been pooled to give an overall average figure in the last column of the table.

Table 28 Effect of Position and Use: Ansell PVC gloves

Use	Index	Statistic	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	Mean
New	BT	Count	23	11		23	6	7		8		15	13
New	BT	UCL	1820	1523		2689	1069	1090		867		309	1338
New	BT	LCL	787	1189		1289	903	845		720		225	851
New	BT	Mean	1033	1356		1400	986	967		793		267	972
New	LT	Count	23	11		23	6	7		8		15	13
New	LT	UCL	3468	2384		4715	2140	2306		1662		1083	2537
New	LT	LCL	1550	2117		2308	2007	2119		1463		889	1779
New	LT	Mean	1918	2250		2406	2073	2213		1562		986	1916
New	SSPR	Count	23	11		23	6	7		8		15	13
New	SSPR	UCL	60	19		36	33	42		55		60	44
New	SSPR	LCL	26	14		17	29	36		51		57	33
New	SSPR	Mean	34	16		19	31	39		53		59	36
New	INT20	Count	23	11		23	6	7		8		15	13
New	INT20	UCL	14304	567		627	2466	2167		4562		25854	7221
New	INT20	LCL	4327	220		269	848	1124		2398		19103	4041
New	INT20	Mean	9977	393		358	1657	1646		3480		22479	5713
New	INT30	Count	23	11		23	6	7		8		15	13
New	INT30	UCL	33216	3180		3454	7969	8154		24967		56418	19623
New	INT30	LCL	10555	1298		1469	4824	4623		17192		47206	12452
New	INT30	Mean	22661	2239		1985	6396	6388		21079		51812	16080
Used	BT	Count	15	8	8		7	9	23	14			12
Used	BT	UCL	1137	1545	494		896	927	636	740			911
Used	BT	LCL	933	1265	316		678	733	510	494			704
Used	BT	Av	1035	1405	405		787	830	573	617			807
Used	LT	Count	15	8	8		7	9	23	14			12
Used	LT	UCL	2068	2490	1911		1685	1767	1372	1479			1825
Used	LT	LCL	1869	2250	1754		1379	1506	1146	1139			1578
Used	LT	Av	1969	2370	1833		1532	1636	1259	1309			1701
Used	SSPR	Count	15	8	8		7	9	23	14			12
Used	SSPR	UCL	43	36	45		48	48	46	49			45
Used	SSPR	LCL	38	26	40		46	44	38	47			40
Used	SSPR	Av	40	31	43		47	46	42	48			43
Used	INT20	Count	15	8	8		7	9	23	14			12
Used	INT20	UCL	3127	1421	9696		7660	6173	11380	13464			7560
Used	INT20	LCL	2026	502	5745		3461	2656	6952	6603			3992
Used	INT20	Av	2577	962	7720		5560	4415	9166	10034			5776
Used	INT30	Count	15	8	8		7	9	23	14			12
Used	INT30	UCL	13458	5301	25034		29445	22807	33751	36414			23744
Used	INT30	LCL	9619	2846	18608		18581	15522	24097	23458			16104
Used	INT30	Av	11538	4074	21821		24013	19164	28924	29936			19924

The figures below shows some of this data in a graphical form. The data is first shown plotted against position, then New vs Used for matched positions. In “position”, an average of around eight pairs of measurements represents each plot.. (It would be desirable to show the confidence limits associated with each measurement so that each point had an cross showing the uncertainty of the position, but a suitable plotting package was not found.) It is possible that a linear relationship exists, but the outliers need explanation. If there was a consistent effect over the surface of the glove with use, then the line would expect to go through the origin. There appears to be a consistent effect, but it is appears to have two components giving a shift and a change of slope. An explanation for this is being investigated in light of the patterns seen for the other indices.

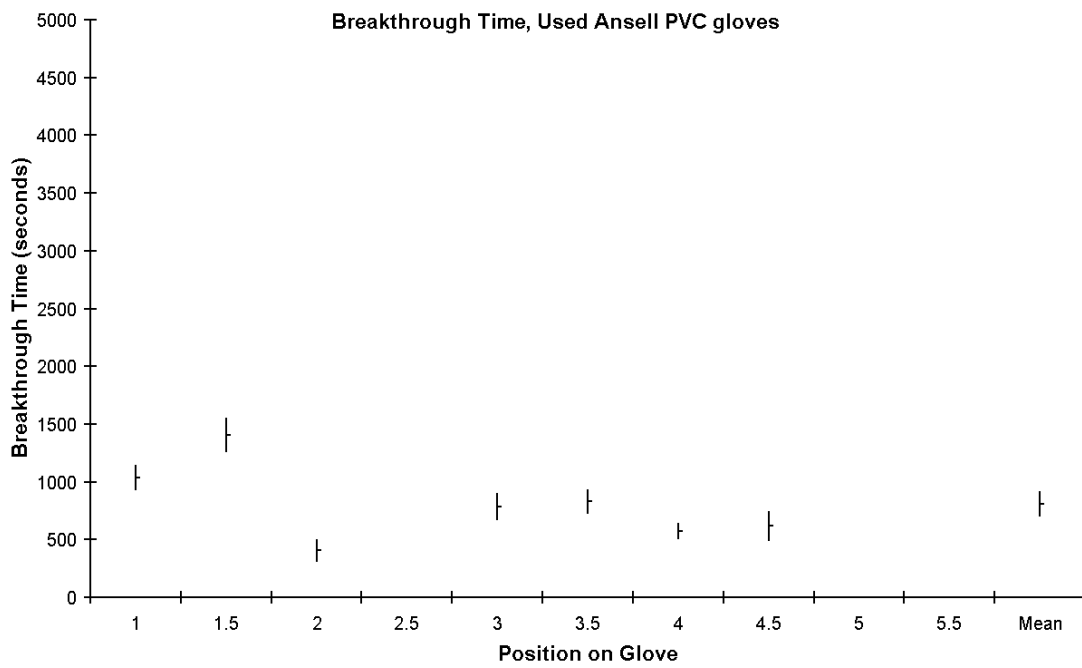
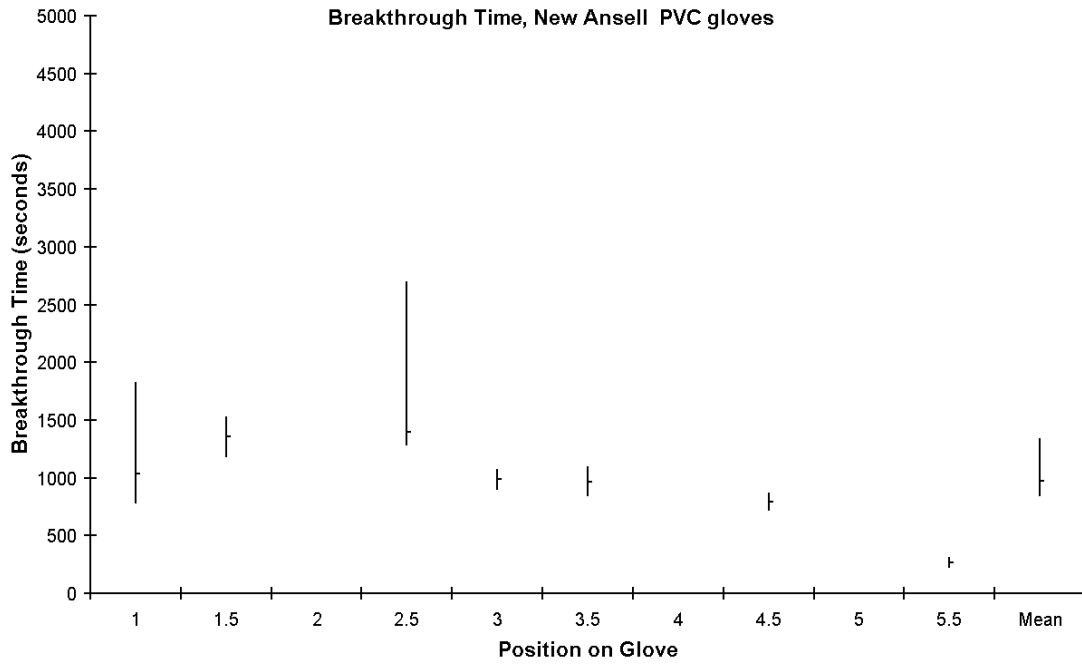


Figure 38 BT - New and Used Ansell PVC gloves

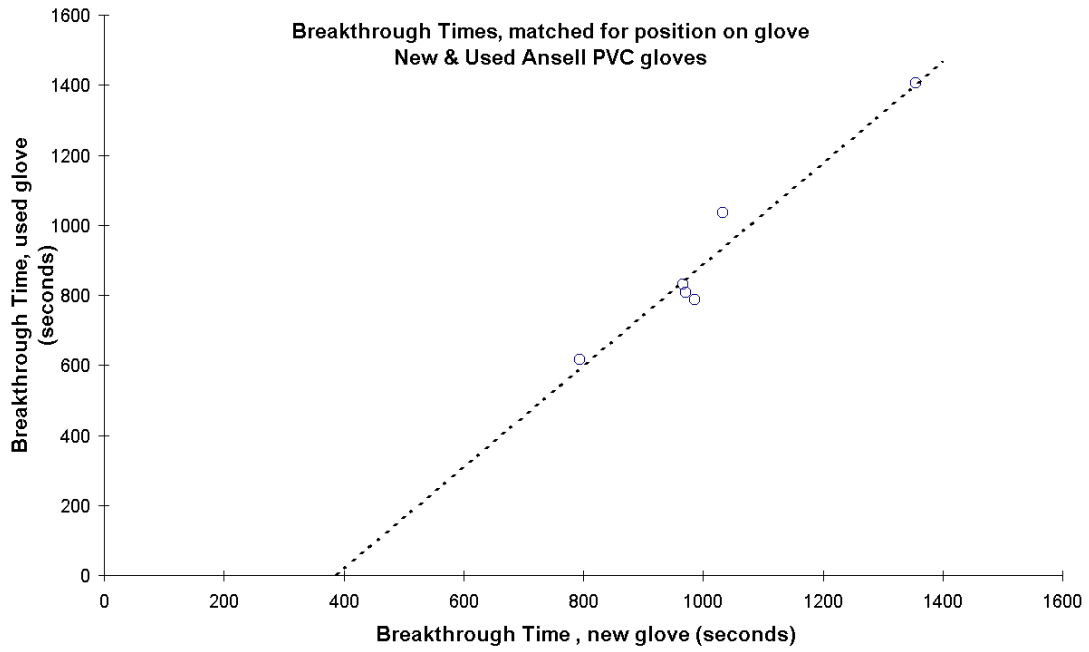
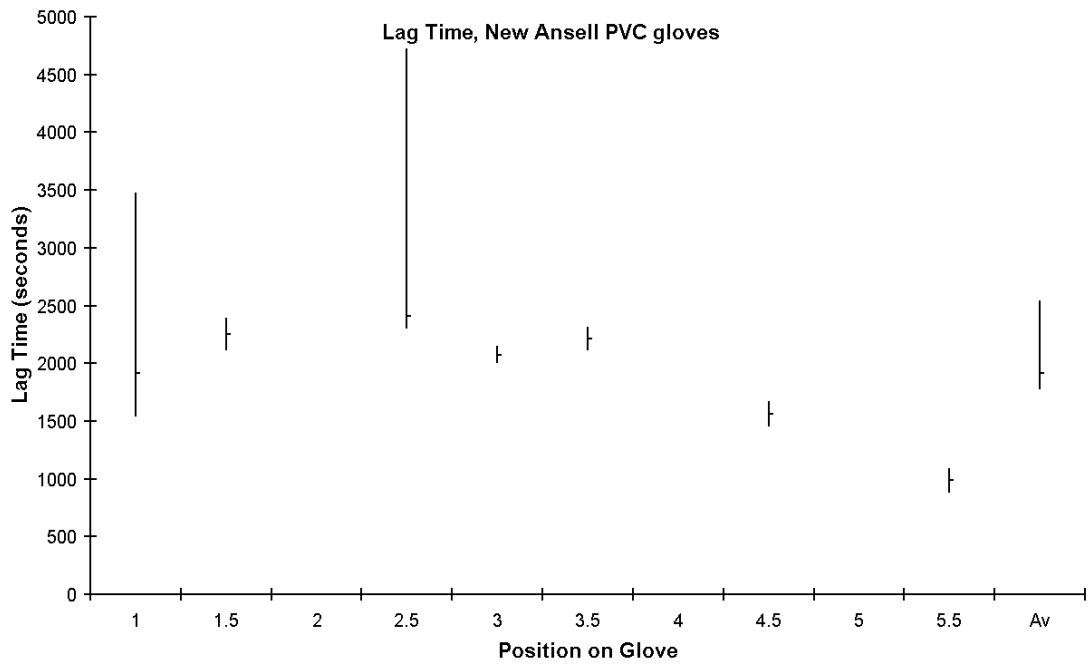


Figure 38 New and Used BT, matched for position

A similar approach can be taken for the other indices. Below, LT gets the same treatment.



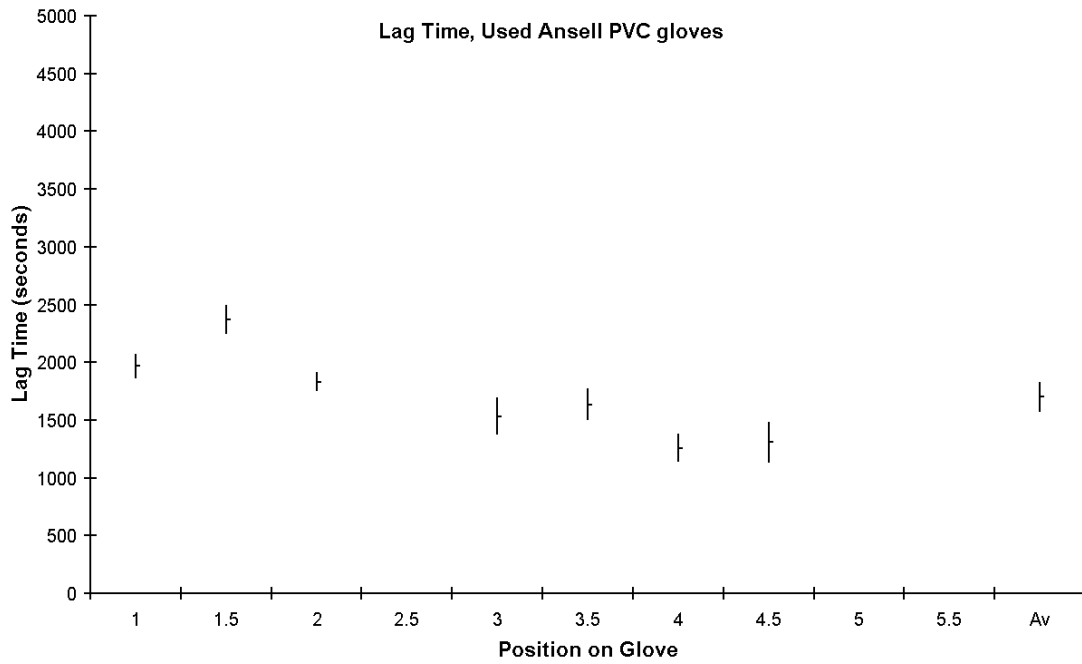


Figure 39 LT - New and Used Ansell PVC gloves

In “Figure 41 New and Used LT, matched for position” below there is a similar plot for LT, but there is a less distinct linear relationship between the data.

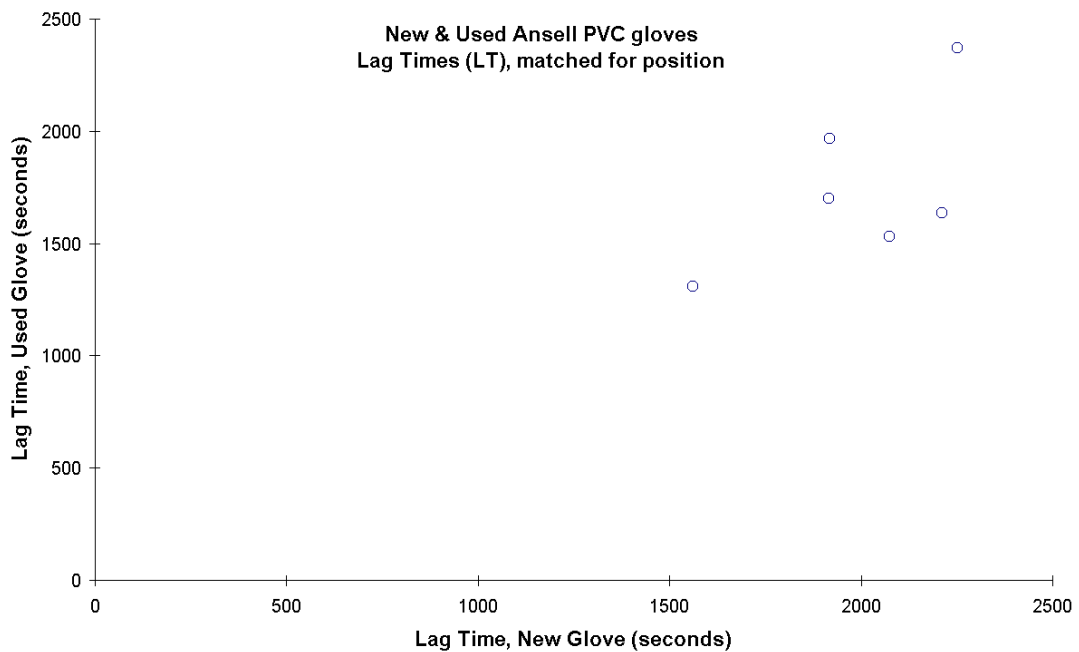


Figure 41 New and Used LT, matched for position

For the Steady State Permeation Rate, the variation with position for new and used Ansell PVC gloves is shown below

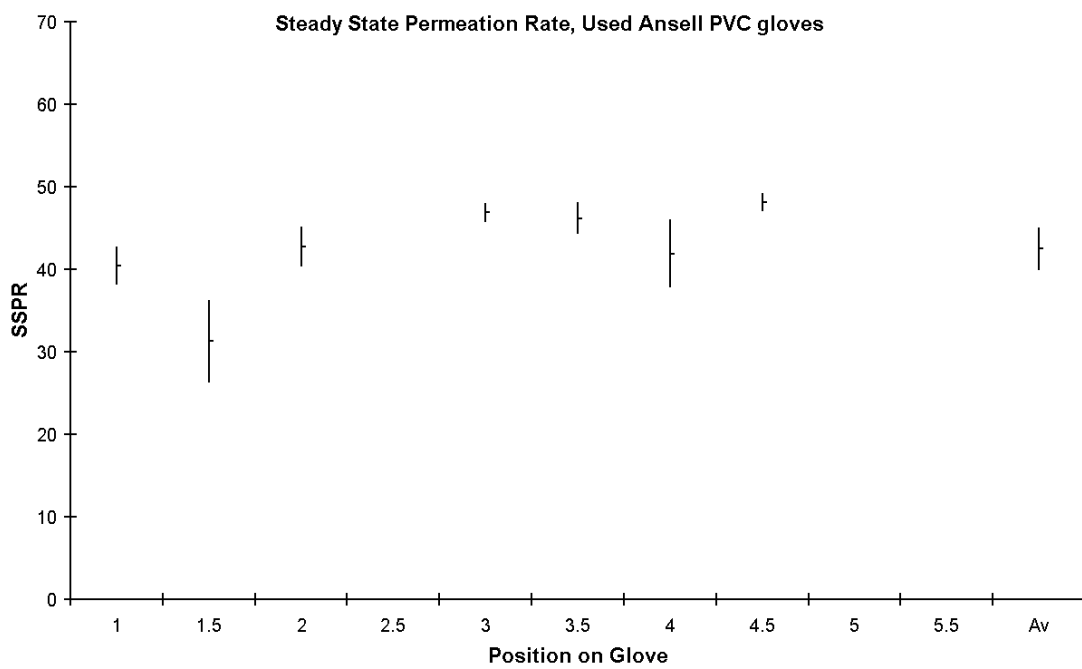
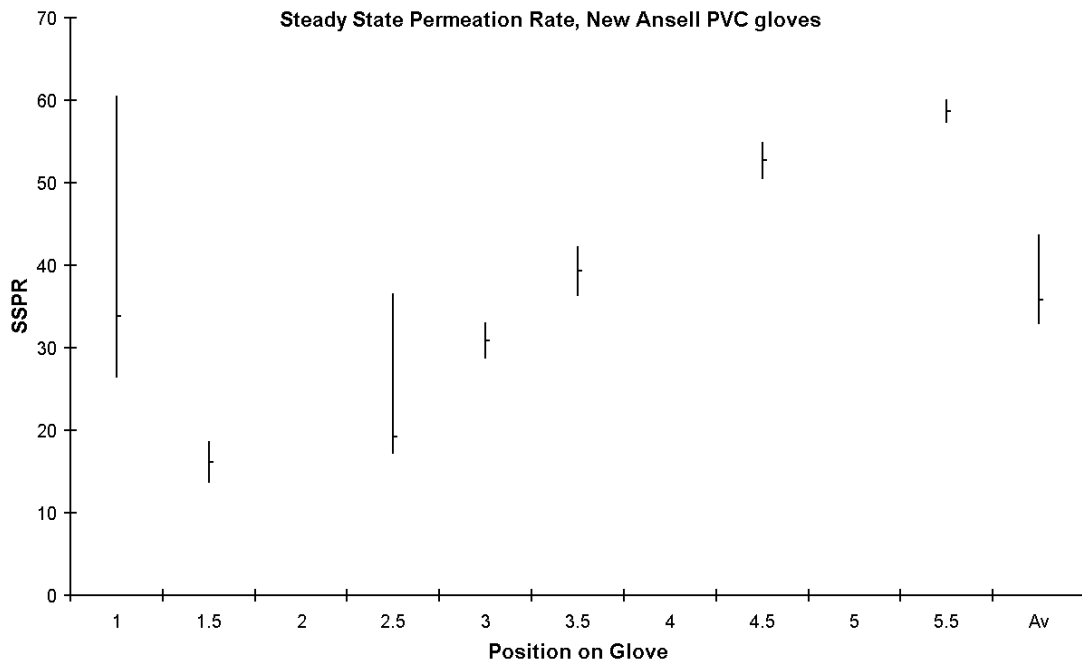


Figure 41 SSPR - New and Used Ansell PVC gloves

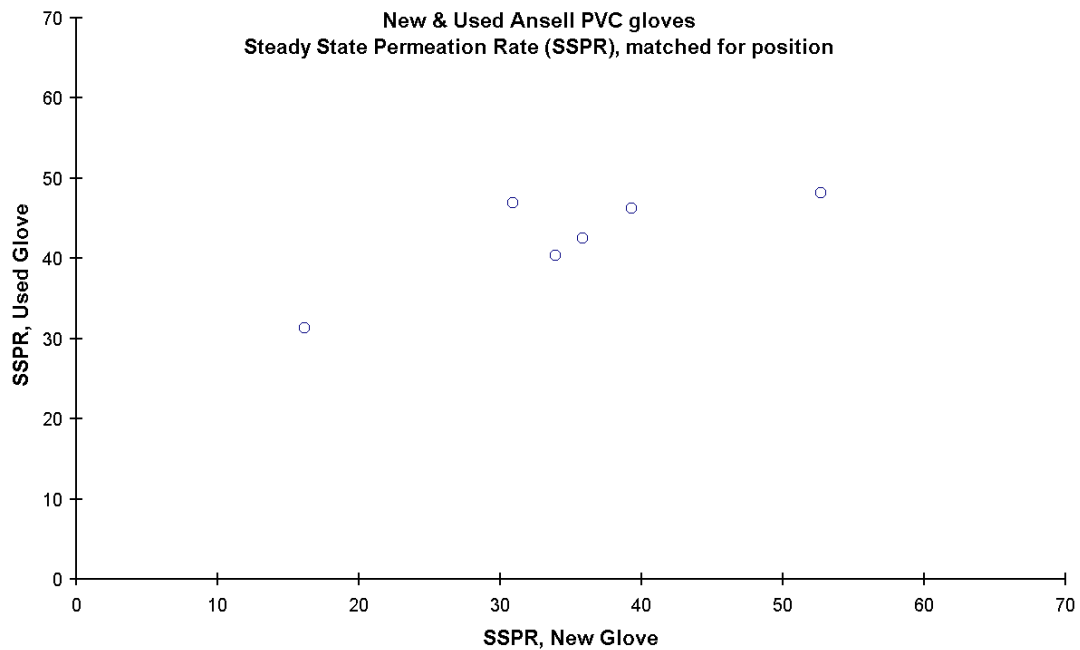


Figure 42 New and Used SSPR, matched for Position

In the figure below, same treatment is given to the two integral permeation indices for new and used (Code 2B) Ansell PVC gloves. The Int20 and Int30 have been plotted on a different scale to make comparison easier. Essentially the same pattern is seen for both, but the differences between new and used are not explicable

Table 29 Integral Permeation: New and Used Ansell PVC gloves by Position

Use	Index	Statistic	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	Av
New	INT20	Count	23	11		23	6	7		8		15	13
New	INT20	UCL	14304	567		627	2466	2167		4562		25854	7221
New	INT20	LCL	4327	220		269	848	1124		2398		19103	4041
New	INT20	Mean	9977	393		358	1657	1646		3480		22479	5713
New	INT30	Count	23	11		23	6	7		8		15	13
New	INT30	UCL	33216	3180		3454	7969	8154		24967		56418	19623
New	INT30	LCL	10555	1298		1469	4824	4623		17192		47206	12452
New	INT30	Mean	22661	2239		1985	6396	6388		21079		51812	16080
Used	INT20	Count	15	8	8		7	9	23	14			12
Used	INT20	UCL	3127	1421	9696		7660	6173	11380	13464			7560
Used	INT20	LCL	2026	502	5745		3461	2656	6952	6603			3992
Used	INT20	Av	2577	962	7720		5560	4415	9166	10034			5776
Used	INT30	Count	15	8	8		7	9	23	14			12
Used	INT30	UCL	13458	5301	25034		29445	22807	33751	36414			23744
Used	INT30	LCL	9619	2846	18608		18581	15522	24097	23458			16104
Used	INT30	Av	11538	4074	21821		24013	19164	28924	29936			19924

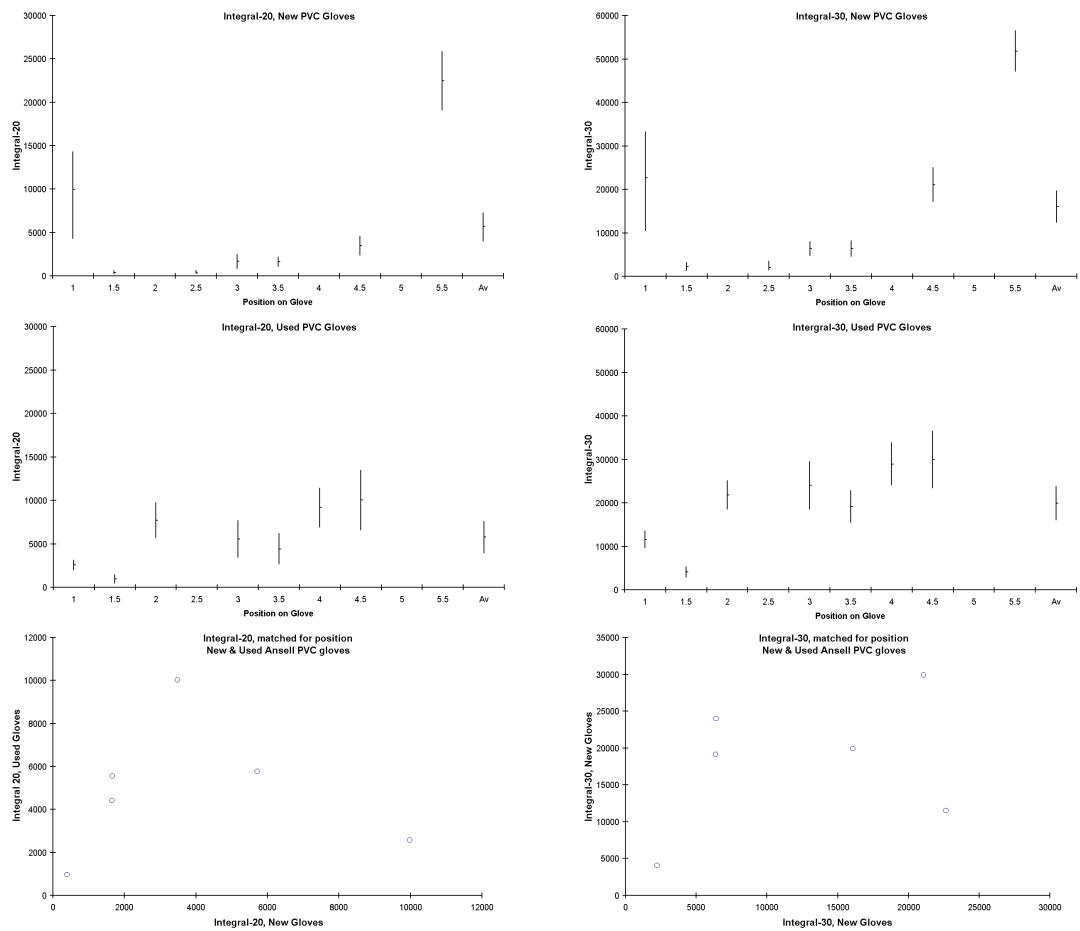


Figure 43 New and Used Integral Permeations

11.4. Qualitative

Investigating reasons for use and discard of gloves was not an intended part of the project, so the investigations can only be considered indicative. On return of the gloves after use, the users were asked about the performance of the gloves and why they discarded them. This information was collected on field worksheets. A worksheet is included in Appendix H “Main Trials”.

Table 30 Comments on glove use

Company	Glove	Task	Failure	Effective	Gloves per day	Reason for discard, comment
Paint	Ansell single dipped PVC gauntlet	Moving pots, acetone, MEK, MIBK, "cleaning solvent"	Right glove, webs and fingertips	Doesn't know	4-5	Visible failure/ Solvent smell on hands
		Paint Mixing & Batching. Protection against paint pigments	No	Yes	1	End of shift
		change bags, solvent wash	No	Yes	1	End of shift
		Epoxy paint clean-up, toluene, acetone, "cleaning solvent"	No	Yes	-	one job, "paint runs down glove when working overhead, then into glove the other way"
Petro 1	Latex rubber	Squeeze bag out, solvent based paint, then wash with "cleaning solvent"	No	Yes	1-2	one job
		lab tests, fuel oils, petrol	Yes	No	5-10	keep hands clean, kerosene caused failure at fingertips
Petro 1	MSA PVC	alkylation plant, Turning valves HF.	No	Yes	Keep 2-3 weeks	Bicarb wash, air dry.

The table above and unwritten observations show that there is a perception of effectiveness was directly related to the lack of visible damage. Smell on hands was used as an indicator of failure. There was no set life time for gloves and there was an expectation that some tasks would require a number of changes of glove. All these indicators point towards a lack of selection for glove performance and a notion that gloves either give 100% protection or no protection (failure). The reality is that any glove will give some protection for a limited duration. The only question is whether the degree of protection is adequate to prevent local effects (dermatitis) or systemic effects which may or may not produce local effects.

11.5. Variation of Weight and Thickness

A decision was made early in the project not to record thickness or weight for supported gloves. The reason for this was that the supporting cloth material would be expected to give a wide variation in thickness unrelated to the thickness of polymer. Part of this would be due to the variations in the thickness of the cloth and part of this would be related to the degree of penetration of the polymer into the cloth during the dipping process during manufacture. Weight could have been used, particularly as a microbalance (Sartorius M5) became available half way through the project. The problem with weighing supported sample after testing would be to ensure consistent sample preparation - the cloth support would tend to wick any solvent as it was removed from the test cell.

As most of the trials involved supported gloves and we found anomalous changes in performance with the sample position, it was an unfortunate decision, as some of this variation may have been attributable to thickness. However, the gloves from which the samples were taken are all labelled and stored, so it should be possible to take samples from them at a later date.

The data below is for ten samples taken from the cuff of a supported Single Dipped PVC gauntlet of Chinese origin.. The thickness was measured with a workshop micrometer (0.01 mm) and the thickness measured with a microbalance (Sartorius M5). Care was taken with the micrometer to ensure a reproducible pressure was placed by the anvils on the sample, as it was easy to compress. This was done by using the spring loaded tightening mechanism and rotating it 3 clicks, a very gentle pressure). The calibration of the microbalance was checked with a calibration certified stainless steel calibration weight. No air density corrections were made. Error from the balance may be discounted as a significant source of error.

Table 31 Sartorius M5 Balance calibration

Calibration Weight (µg)	Certified (µg)
4997042	4997033

The error in measurement of the certified weight (~5 g) was 9 micrograms. This error is insignificant in these trials, but would have been reduced if air density corrections had been made.

Table 32 Variation of Thickness and Weight of samples from same part of PVC glove

Sample	Weight (mg)	1	2	3	4	5	Mean Thickness (µm)	Standard Deviation	Location	Cell
1	416.693	320	325	305	290	320	312	14	Cuff	Large
2	429.380	330	325	295	320	315	317	14	Cuff	Large
3	484.974	420	400	415	370	390	399	20	Cuff	Large
4	447.766	325	315	325	310	300	315	11	Cuff	Large
5	425.985	310	325	300	295	305	307	12	Cuff	Large
6	482.192	395	430	400	385	445	411	25	Cuff	Large
7	479.990	370	370	415	365	380	380	20	Cuff	Large
8	509.138	430	460	455	470	450	453	15	Cuff	Large
9	482.366	455	390	460	395	450	430	34	Cuff	Large
10	462.882	405	410	370	375	385	389	18	Cuff	Large
Mean	462.137						371.300			
SDev	30.755						54.388			
11	133.087	355	365	400	355	405	376	25	Cuff	Small
12	131.803	365	365	345	365	410	370	24	Cuff	Small
13	140.509	475	455	465	475	450	464	11	Cuff	Small
14	138.810	375	405	385	385	390	388	11	Cuff	Small
15	138.060	465	420	465	430	480	452	26	Cuff	Small
16	133.325	370	345	340	335	360	350	15	Cuff	Small
17	136.015	380	435	430	445	405	419	26	Cuff	Small
18	137.019	365	355	360	355	335	354	11	Cuff	Small
19	128.460	295	295	310	305	310	303	8	Cuff	Small
20	136.296	300	305	290	305	295	299	7	Cuff	Small
Mean	135.338						377.500			
SDev	3.641						55.722			

In the table above, note that the standard error (SD/Mean) of the weight is 3.6 to 6.5%, but for the thickness the standard error is 15%. As the weighing was precise and accurate, the variation in the weights could be attributed to

- real differences in polymer thickness,
- variations in the amount of fabric support on the samples, and
- variations in the size of the sample cut with the sharp metal wad punch.

A pessimistic view would be to attribute all the variation to differences in real polymer thickness. This would only account for a fraction of the variation in the thickness as measured by the micrometer. The reasons for this variation are not known, but possible reasons are discussed below.

Figure 44 and Figure 45 below show the data from Table 32 above. If the thickness was a true thickness, then the line would be expected to pass through the origin. As the fabric bulks out the thickness, it appears that the true thickness is about 400 µm for the Large Cell and 900 µm for the

small cell, less than the recorded thickness (the “Y” intercept) This interpretation - a measurement showing half the real thickness is not likely, as squashing of the sample to half its thickness would have been observed. A repeat of the tests with another micrometer, unsupported glove and material of more uniform thickness would give more confidence in the result.

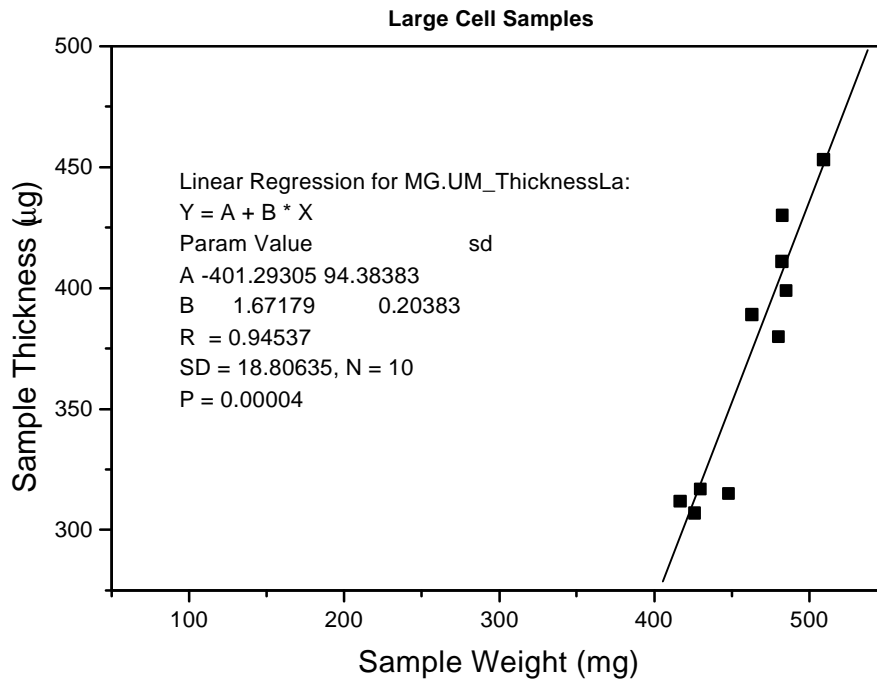


Figure 44 Large Cell: Variation of sample Thickness and Weight

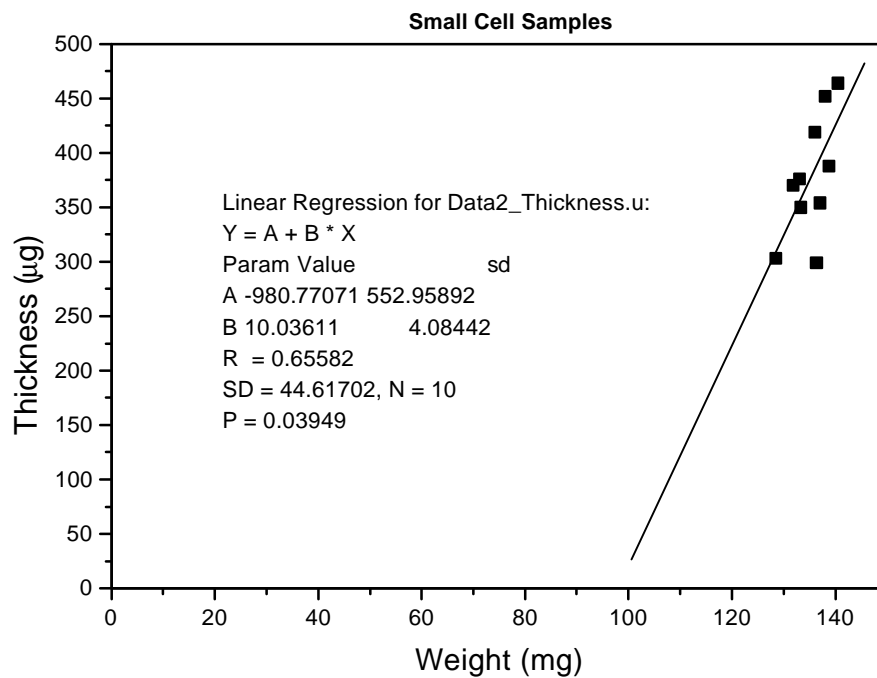


Figure 45 Small Cell: Variation of sample Thickness and Weight

While thickness may be a useful parameter to model diffusion processes, a measurement of true thickness appears difficult, if the apparent true thickness is negative. Whatever the reasons for discrepancies between thickness and weight, it does indicate that thickness measurements for gloves, and corrections for thickness to allow glove performance to be compared has to be done with great care and the technique of measuring thickness has to be validated.

11.6. Mixtures

The following trials were done with the Perkin Elmer 1750 FTIR Spectrophotometer. Ten scans at 4 cm⁻¹ resolution were performed from 600 - 4000 cm⁻¹, using the Griffith Large Cell. A record of the permeation was also made with the *GloveTest* rig using the HNU photoionisation detector.

Table 33 Mixtures for FTIR Trials

Solvent mix	Times of scans (minutes)	Comment
hexane	0, 20, 60, 90	BT at 20 min evident
1:1:1 hexane, toluene, acetone	0, 5, 10, 15, 20, 25, 40	
1:1 toluene, hexane	0, 10, 20, 30, 40, 50, 70, 131	
60:40 hexane, toluene	0, 10, 20, 30, 40, 50, 100	
60:40 hexane, toluene	0, 10, 20, 30, 40, 60	
acetone	0, 6, 9, 25, 30, 35	

As previously noted, we were unable to extract the spectral data from the runs on our computer. We will have to gain access to the FTIR again, reload the data and try to extract the data in a form we can analyse.

There is a great potential to make a permanent link to a cheap FTIR machine. An appropriate gas cell with a low volume would have to be chosen, and the *GloveTest* software and the FTIR control and output synchronised, but this would provide very fast and detailed information on mixtures permeating a glove which could not easily be matched by existing sampling techniques such as gas chromatography. Further work could also be made using the Bruel and Kjaer 1302 photo-acoustic spectrophotometer, but again, linking control software would have to be developed and the purchase of additional interference filters would have to be contemplated to analyse a range of solvents.

11.7. DSC Trials

Differential Scanning Calorimetry (DSC) is one of the most widely used thermal analysis techniques to compare the thermal properties of samples. The technique works by subjecting a sample and a reference cell to a precisely programmed temperature change whilst keeping both cells at the same temperature. When one of the samples in a cell has a “thermal transition” or it adsorbs or emits energy due to a chemical or physical change that cell requires more or less energy than the other to maintain the same temperature. The difference in heating is recorded. The analysis technique is very sensitive and uses a sample size of 10 to 100 mg. The technique is used extensively within the polymer science, material science and metallurgy/geology for the analysis of reaction kinetics, purity analysis and the following of polymer curing processes.

The tools of polymer science have not been widely applied to gain insights to the performance of gloves and there is no mention of DSC being used for this (or any other purpose) in the occupational hygiene literature

Tests were performed using new and permeation tested Single Dipped PVC glove samples. The exposure history of the permeation tested samples was under controlled conditions in the *GloveTest* rig, so the exact type of solvent and the exposure time was known. The DSC temperature programme was from 275 °K to 340 °K

The DSC operating conditions were:

- Programme 300-420 °K
- Range 5 mcal/sec
- Heating Range 10 °K/min
- Chart speed 1 cm/min

PVC in its pure state should have a **glass transition temperature**, T_g at about 340 °K. This is not a well defined point because of the amorphous nature of the polymer. Typically amorphous materials display less of a thermal profile compared to crystalline or semi-crystalline structures. The PVC glove material contains any number of fillers pigments and plasticisers. These additives will have an effect on the overall thermal profile of the material. The plasticisers in PVC lower the T_g to below 270 °K effectively making a hard brittle material (familiar in PVC drain and water pipes) into a flexible rubber type material. To achieve this flexible rubber material from PVC up to 50% by weight of the rubberised polymer is plasticiser which is mechanically rather than chemically mixed with the PVC polymer molecules.

The temperatures in our experiments were not low enough temperature to observe the T_g of the rubberised PVC, which would have occurred below 270 °K. A coolant (liquid nitrogen/acetone mix ~200 °K) would be needed to attain cooling to the level of 250 °K. As expected, the PVC material did not display a large variation in its thermal profile. There was a slight exotherm for the new gloves at 340 °K. This exotherm shifted approximately 10 degrees higher with the used gloves to 350 °K. The exotherm observed was a gentle change which indicates a physical process rather than a chemical or phase change, indicating that there is some physical differences between an exposed and new glove. The thermal change shown was likely to be caused by the removal of plasticiser /solvents from the new glove with heating. The shift with the solvent exposed gloves was likely to be due to encapsulated solvent still in the glove material. The lack of a lower peak in the exposed gloves showed that the solvent exposure removed most of the original plasticiser /solvent material and replaced it with the exposure solvent.. The material displayed another sharp peak between 387-390 °K which indicated the melting point (T_m) of the PVC material. This peak was observed on all samples regardless of exposure. No new information would have been gained progressing past this melt point and it was most likely that some of the plasticiser had been displaced by solvent in the system or that there was still solvent in the sample.

Further work in this area could be to use a lower temperature profile and then observe any trends in T_g with solvent exposure. To carry this even further, the use of TGA FTIR (Thermo Gravimetric Analysis - Fourier Transform Infra Red) would allow accurate plotting of the weight loss of a sample throughout a temperature profile and analysis of the evolved gasses with FTIR. This would give many insights into the processes involved in glove permeation.

12. DISCUSSION

12.1. Existing guidelines

The rational selection of approach in the workplace will depend on cost of setting up a selection process, complexity of the choice, and ability to understand the factors which affect glove performance. With a professionalising of Occupational Health and Safety in Australia - reflected by the growth of numbers of tertiary courses and membership of professional occupational health and safety bodies, an desire to make professional judgements in the selection of gloves will undoubtable grow. To properly understand the protective properties of gloves, some understanding of chemistry and physics is required, skills that a trade based safety officer or a safety manager with a background in industrial relations may not have acquired. Respiratory protection and hearing protection programs are well established in many industries, and a similar or better approach should be made with gloves or chemical protective clothing in general.

This project has revealed that selection in industries where contact with solvent is common is not based on the best glove for the job. PVC gloves were used for heavy work and vinyl gloves were used for work where tactility was important, such as in the laboratory. In the laboratory, severe degradation of the vinyl gloves was reported with some solvents, and the PVC gloves showed significant permeation in less than 20 minutes. PVC gloves were also used in the petrochemical industries, but acid contact rather than solvent contact was likely.

Overall a glove selection and use program requires the technical performance information from manufacturers so that a selection based on an understanding of the permeation processes can be made with judgements being made where the information is incomplete, such as the permeation of mixtures. Selection is still a process of eliminating bad choices, with little information to guide the best choice. Once manufacturer's start to publish more useful information of the performance of their gloves such as the 3-DSP, then more rational choices can be made. There will still be a large gap between the knowledge required to make a good decision, but information already available is not being applied. This project adds additional factors which are discussed below.

12.2. New vs Used

The project sought to find out the effect of Use on glove performance. To do this a new biopsy cell, the Griffith Small Cell was developed, to go where no testing cell had gone before - away from the palm and cuff of the glove. The reasons for glove choice were found to be different than expected - cost and protection from chemical and old sweat smells on the skin, so the plan of sampling at geometric intervals 2, 4 8+ hours of use was abandoned. In looking for the effect of use on different parts of gloves from the fingers to the cuff and along the front and back of gloves it was discovered that Position was a greater factor than Use in the performance of gloves.

In the Results of the Pilot Trials and Main Trials, a representative selection of the data showed that Use affected the front of gloves more than the back by something like a factor of two, but only in places where direct contact with chemicals and mechanical damage would be expected to occur - the fingers and palm.

12.3. Front-Back

There was occasionally a difference between the front and back of gloves, particularly in the cuff region. This may be explicable by greater variations in thickness in this area, but reliable estimates of true thickness will have to be developed. Micrometer measurements with supported gloves did not appear to be reliable.

12.4. Fingers to Cuff

A distinct and statistically significant monotonic gradient between fingers and cuff has been demonstrated with some gloves. In at least one glove, anomalous permeation was seen in the finger region of a new glove. This demonstrates that confidence in the performance of a glove has to be based not just on the published figures for a glove, but in knowledge of how much variability there is between gloves and between batches of gloves. More expensive PVC gloves like the MSA Metalguard

showed very little variation between fingers and cuff, and very little variation between samples at each location. This has to be related to quality control in manufacture.

12.5. Use and Position

When the variables of Glove Type, Use and Position were investigated using unbalanced correlation analysis (SAS General Linear Model), the combination of these three parameters explained most of the variation in the most important indices.

Table 34 Effect of Glove Type, Position and Use on Performance Indices

Index	r ²
Midpoint Time	56
Midpoint Value	27
Slope	57
Intercept	58
Breakthrough Time	62
Max Point	72
Max Time	53
Top Slope	24
Top Intercept	66
Steady State Permeation Rate	67
Lag Time	61
Integral_20 min	59
Integral_30 min	63

Here the less useful and unstable indices such as Top Slope have only 24% of their variation explicable by Glove Type, Use and Position, whereas the index Max Point - the maximum permeation rate, outperforms the other indices as 72% of its variation is explicable by Glove Type, Use and Position. Surprisingly, BT and LT perform similarly, and Integral 20 and Integral30 does not perform as well as the SSPR.

12.6. Solvent

The effect of solvent was not investigated to the degree that was planned, particularly as there were plans to model the effects of mixtures. There were some early measurements performed with hexane, but the numbers were not sufficient nor the documentation of position for this to be of any use.

12.7. Mixtures

A number of combinations of toluene, hexane and acetone were tried in a Griffith Large Cell with new supported PVC glove material, using FTIR techniques to analyse the permeation process. There were difficulties in extracting the data from the spectra, and the data still awaits analysis. The technique shows promise, but only if directly coupled to the *GloveTest* rig so that automated analysis can be performed. This would be a complex task, but not impossible.

12.8. Australian vs Imported

As mentioned, there was less variation over the surface of Australian made gloves than cheaper imported gloves, and the permeation was less. This would indicate that permeation figures based on standard measurements on the palm would be indicative of the performance of the whole glove, so it is more likely that a known degree of protection would be obtained.

12.9. Relevance of Test Results

The selection and use of gloves to protect from the effects of chemicals in the workplace is a complex problem. The chemicals have to be known, a glove must be chosen for its protective properties against the chemical or formulation of chemicals. Real exposure is likely to be intermittent, with drying of the glove between each contact with the chemical. Mechanical forces complicate the process and temperature and temperature gradients make a mathematical solution of the diffusion process very hard to estimate. Added to this the variation in skin thickness, great uncertainties in the uptake through the skin and predicting the actual chemical exposure for a task becomes a very difficult to estimate with useful certainty. Add again to this individual variation in response to chemicals and it is near impossible to set exposure guidelines which will protect most individuals from adverse health effects for a working lifetime.

The present approach is to try to eliminate the worst glove choices, in the hope that what is left will give better protection. The experimental results from this project will only contribute a small amount to allowing a better choice of gloves and guide better use practices. The results do point to:

- previously unknown variations with Position along a glove,
- the lesser effect of Use than Position
- A range of possible indices, including a simple measure of maximum permeation rate.
- The possibility (demonstrated) of automating the testing process
- The complexities of concentration dependent diffusion
- Biopsy methods of glove testing with the Griffith Small Cell
- Intermittent exposure testing of gloves with the Bromwich-Smith Intermittent Cell.
- The problems associated with poor statistics in choosing between gloves

12.10. Validation and calibrations

Calibration of the flow sensor, temperature sensor and photoionisation detector were performed and are believed to be reliable. Validation of the Griffith Small Cell, Griffith Large Cell against the standard ASTM cell was only partially successful. The exposed areas of the samples was different for each cell, and the flow relates through the cells were different but appropriate. Additional diluting flows were added after the cells to keep similar concentrations in the effluent flow being sampled by the photoionisation detector. Everything else was the same. Additional work will have to be done to trace the source of discrepancy between the permeation rates - the difference is systematic. There is an importance difference in that the smaller the cell, the flatter the “steady state” portion of the permeation curve. The reasons for this are not known, but it may be that the smaller sample is more constrained, so mechanical effects from distortion of the sample when it swells with solvent are greater for the larger cells. Whether this is desirable as it may better represent the geometry of a glove during use, is unresolved.

12.11. Were Aims and Objectives met?

The stated aim of this study was to “*develop guidelines for the safe use of chemical gloves in the workplace*”. This aim was ambitious was found to build on existing comprehensive rules published by the National Safety Council. Significant findings were made in developing the technology of testing, with the development of sophisticated GloveTest software and simple but effective cells. The most significant findings were that sample position was a greater factor than glove usage in changes in permeation rate and that the selection of gloves based on published data is probably flawed as the number of test does not allow rational selection between all but the most disparate performing gloves. Ongoing work will be able to utilise an “intermittent” cell, developed to simulate intermittent exposure in the workplace. Guidelines based on recent research and polymer science show that glove thickness combined with temperature of hands and solvent or workplace to have special effects on diffusion through gloves. We consider that the aims of the study were met.

The stated objectives of the project were to be able to answer the following questions:

1. *At what rate do the protective properties of chemical gloves change with actual workplace use?*
2. *What are the mechanisms of permeation and degradation and how does the pattern of exposure affect these changes.*

As these were based on unstated assumptions these were modified to

- 1. How do the protective properties of chemical gloves change with actual workplace use?*
- 2. What are the mechanisms of permeation and degradation and how does use affect these changes?*

The first objective was met, though only some of the gloves were analysed. There is much room for further research. The second objective was partially met in that the literature review revealed much about the processes, but the experiments with mixtures were not completed and the subsequent modelling was not performed. Overall, the amount of work done was quite large and some of the findings were quite unexpected, particularly the significant role of sample position in glove permeation. The largely unexplored link with polymer science and work in progress should be very fruitful in allowing selection of the best glove for a task rather than just eliminate the worst choices.

13. RECOMMENDATIONS

These recommendations are based on the survey of the literature, including several recent PhD theses; a review of published guidelines and rules; and research results from this project.

13.1. User Recommendations

1. Ensure the carrier solvent in formulations such as pesticides are compatible with the glove
2. Choose a glove of the greatest thickness compatible with adequate tactility to get the greatest temperature insulating effect from the heat of the hands.
3. Choose Australian made rather than cheap imported gloves. They give better protection.
4. For short task (minutes, rather than 10's of minutes, any glove that does not visibly degrade should give some protection. Softening of a glove is a sign of permeation.
5. Performance of the same glove type between brands is significant and may relate to thickness.
6. Selection between gloves on the basis of Breakthrough time may only be sound if the Breakthrough times are different by a factor of two, as lesser real differences cannot be detected under present testing protocols.
7. Follow the rules in Appendix E.

13.2. Technical Recommendations

1. Perform tests based on sound statistical principles, not the nominal duplicate recommended by standards. Without a firm statistical base, it is not possible to say with certainty that one glove is better than another under set test conditions.
2. Allow the development of newer test cells for permeation testing, but ensure that their performance is validated against a standard cell. This could be the ISO or the ASTM cell.
3. Publish the measured "three dimensional solubility parameter" for gloves to allow a better selection of gloves with unlisted chemicals or mixtures of chemicals.
4. Further investigate the degree of variation between gloves within the same batch and between batches and publish the findings so that users can understand how much difference between gloves is significant.

13.3. Research Recommendations

1. Further investigate indices, particularly ones relating to chemical dose over a shift. This should be coupled with biological monitoring.
2. Investigate the performance of formulations and mixtures using the tools of polymer science to better understand the permeation process and thence predict permeation of mixtures of chemicals
3. Further investigate intermittent exposure and develop the theory to predict the effect of cyclic exposure and drying has on the protective properties of gloves.
4. Investigate the application of the tools and theory used in polymer and membrane science to the performance of gloves.
5. Investigate the relationship between measured glove thickness and glove performance.

14. BIBLIOGRAPHY

1. 4H Chemical Protection Guide 1990/91. Safety 4 A/S Denmark. Oct 1990
2. Aithal U S, Aminabhavi T M "Diffusivity, Permeability and Sorptivity of Aliphatic Alcohols through Polyurethane Membrane at 25, 44 and 60o C" J. Chem. Eng. Data 35 298-303, 1990
3. Aminabhavi T M, Aithal U S, Shukla S S "An Overview of the Theoretical Models Used to Predict Transport of Small Molecules through Polymer Membranes" JMS-Rev. Macromol. Chem. Phys C28(3&4) 421-474, 1988
4. Aminabhavi T M, Harogoppad S B "Kinetic and Thermodynamic Study on the Sorption of Liquids by Polymer Films" J Chem Education 68 (4), 343-346, 1991
5. Aminabhavi T M, Harogoppad S B, Khinnavar R S "Diffusion and sorption of Organic Liquids through Polymer Membranes. III. Polyurethane, Neoprene, SBR, EPDM, NBR, and Natural Rubber versus Cyclic Compounds, Esters and Hydrocarbons" Polym.-Plast. Technol. Eng 30(5&6) 453-472, 1991
6. Aminabhavi T M, Khinnavar R S "Diffusion and sorption of organic liquids through polymer membranes: 10. Polyurethane, nitrile-butadiene rubber and epichlorohydrin versus aliphatic alcohols (C1-C5)" Polymer 34(5) 1006-1017, 1993
7. Ansell Edmont Chemical Resistance Guide, 5th Edition. Ansell Edmont 1990
8. ASTM F739-85 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases. American Society for Testing of Materials, 1986
9. ASTM F903-87 Standard Test Method for Resistance of Protective Clothing Materials to Penetration by Liquids. American Society for Testing of Materials, 477-486 1987
10. Australian Standard AS 3765.1-1990 "Clothing for protection against hazardous chemicals. Part 1: Protection against general or specific chemicals" Standards Australia, Sydney, 1990
11. Baker R "Detection of Chemicals that Cause Skin Cancer" National Research Workshop on Occupational Skin Disorders and Occupational Cancer, Sydney, 1991
12. Bensek C K "The Effects of Various Thicknesses of Chemical Protective Gloves on Manual Dexterity" Ergonomics 36(6) 678-696, 1993
13. Berky ZT, Luciano J, James WD "Latex Glove Allergy - A Survey of the US Army Dental Corps" JAMA 268 (19), 2695-2697, 1992
14. Brooks B, Bromwich D W "A New Glove Performance Index" Proceedings of the Twelfth Annual Conference of Australian Institute of Occupational Hygienists Dec, 1993
15. Cvejanovich G J "The vapor permeability and wear resistance of full-body protective garments (Volumes I and II)" PhD Thesis Texas A&M University, 1989
16. DR 93127. Draft Australian/New Zealand Standard for Comment "Industrial Gloves and Mittens" Standards Australia, Sydney. June 1993
17. Forsberg K, Faniadis S "The Permeation of Multi-Component Liquids Through New and Pre-Exposed Glove Materials: Am Ind Hyg Ass J 47(3) 189-193, 1986
18. Fricker C, Hardy J K. "the effect of an alternative environment as a collection medium on the permeation characteristics of solid organics through protective glove materials." Am Ind Hyg Ass J 55(8) 738-742 , 1994
19. Ghosh I, Sanyal S K, Mukherjea R N "Pervaporation of Methanol-Ethylene Glycol with Cellophane Membranes: Performance of Conditioned Membranes" Ind. Eng. Chem. Res. 28 757-763, 1989
20. Hansen C M, Hansen K M "Solubility Parameter Prediction of the Barrier Properties of Chemical Protective Clothing" in Performance of Protective Clothing: Second Symposium, ASTM STP 989, S Z Mansdorf, R Singer, A P Nielson Eds. American Society for Testing and Materials, Philadelphia 197-208 1988
21. Harogoppad S B, Aminabhavi T M "Diffusion and Sorption of Organic Liquids through Polymer Membranes. 5. Neoprene, Styrene-Butadiene-Rubber, Ethylene-Propylene-Diene Terpolymer, and Natural Rubber versus Hydrocarbons (C8-C16)" Macromolecules 24 2598-2605, 1991
22. Harogoppad S B, Aminabhavi T M "Sorption and transport of substituted benzenes into some structurally different engineering polymers" Polymer Communications 32(4) 120- 122, 1991
23. Hassler K D "Factors affecting breakthrough time of commercial pesticide formulations through butyl glove material" PhD Thesis, U of North Carolina at Greensboro, 1989

24. Hirahara K, Takahashi S, Iwata M, Fujimoto T, Miyaki Y "Artificial Membranes from Multiblock Copolymers. 5. Transport Behaviours of Organic and Inorganic Solutes through a Charge-Mosaic Membrane" *Ind. Eng. Chem. Prod. Res. Dev.* 25 305-313, 1986
25. Holmes N "Are Known Preventative Measures for Epoxy Resin Allergic Contact Dermatitis Implemented in the Building and Construction Industry?" 1991 National Research Workshop on Occupational Skin Disorders and Occupational Cancer" *Worksafe Australia, Sydney, July 1991*
26. Jencen DA "Analytical Methods to Evaluate the Permeation Characteristics of Glove Materials Under Various Environmental and Experimental Conditions" PhD Thesis, U Arkon 1989
27. Khinnavar R S, Aminabhavi T M "Diffusion and sorption of organic liquids through polymer membranes. IX. Bromobutyl Rubber, Chlorosulfonated Polyethylene, and Epichlorohydrin versus Substituted Monocyclic Aromatic Liquids" *Polym.-Plast. Technol. Eng.* 31(7&8) 589-606, 1992
28. Leinster P et al "The Development of a Standard Test Method for Determining Permeation of Liquid Chemicals Through Protective Clothing Materials" *Ann Occ Hyg* 30(4) 381-395, 1986
29. Leung H-W, Paustenbach D J "Techniques for Estimating the Percutaneous Absorption of Chemicals Due to Occupational and Environmental Exposure" *App Occ Env Hyg* 9(3) 187-197, 1994
30. Liu R "Three-dimensional quantitative structure-transportability relationships for prediction of membrane flux and a study of solvent effects on conventional predictive models (Volumes I and II)" PhD Thesis, U of Iowa, 1991
31. Lundy K A, Cabasso I "Analysis and Construction of Multilayer Composite Membranes for the Separation of Gas Mixtures" *Ind. Eng. Chem. Res.* 28 742-756, 1989
32. McHugh A J, Yilmaz L "The Diffusion Equations for Polymer Membrane Formation in Ternary Systems" *J. Polym. Sci.: Polym. Phys. Ed.* 23 1271-1274, 1985
33. Mellstrom G A, Landersjo L, Boman A "Permeation of Neoprene Protective Gloves by Acetone: Comparison of Three Different Permeation Cells in an Open Loop System" *Am Ind Hyg Ass J* 50(10) 554-559, 1989
34. Menke R, Chelton C F "Evaluation of Glove Material Resistance to Ethylene Glycol Dimethyl Ether Permeation" *Am Ind Hyg Ass J* 49(8) 386-389, 1988
35. Neogi P, Kim M, Yang Y "Diffusion in Solids under Strain, with Emphasis on Polymer Membranes" *AIChE Journal* 32(7) 1146-1157, 1986
36. Olsen R J et al "Examination Gloves as Barriers to Hand Contamination in Clinical Practice" *JAMA* 270(3) 350-353, 1993
37. PC-10-xx Series User's Manual.(for PLC card). Procon Technology, Melbourne. October, 1992
38. Perkins J L "Chemical Protective Clothing: II. Program Considerations" *App Ind Hyg* 3(1) 1-4, 1988
39. Perkins J L "Chemistry of Chemical Protective Clothing Formulations" ~1993
40. Perkins J L "Decontamination of Protective Clothing" *App Occ Env Hyg* 6(1) 29-35, 1991
41. Perkins J L "Residual spilled solvents in butyl protective clothing and usefulness of decontamination procedures" *App Ind Hyg* 2(5) 179-182, 1987
42. Perkins J L "Solvent-Polymer Interactions" Ch4, ~1993
43. Perkins J L et al, "Skin Protection, Viton, and Solubility Parameters" *Am Ind Hyg Ass J* 47 803-808, 1986
44. Perkins J L, Knight V B "Risk Assessment of Dermal Exposure to Polychlorinated Biphenyls Permeating and Polyvinyl Chloride Glove" *Letter, Am Ind Hyg Ass J* 50 A171-172, 1989
45. Perkins J L, Ridge M C "Use of Infrared Spectroscopy in Permeation Tests" *Special Technical Testing Pub 900, ASTM* 22-31, 1986
46. Perkins J L, Tippit A D "Use of Three-Dimensional Solubility Parameter to Predict Glove Permeation" *Am Ind Hyg Ass J* 46(8) 455-459 1985
47. Raheel M (ed) "Protective Clothing Systems and Materials" Marcel Dekker, 1994
48. Schwoppe A D, Goydan R, Reid R C, Krishnamurthy S "State-of-the-Art Review of Permeation Testing and the Interpretation of Its Results" *Am. Ind. Hyg. Assoc. J.* 49(11) 557-565, 1988
49. Super 12 Bit A/D-D/A Card Manual. Distributed by Procon Technology, Melbourne. Undated
50. Swearingen P M, Johnson J S, Priante S J "Protective Glove Permeation Analysis" Final Report for Allied-Signal Aerospace Company, Kansas City Division ICO Q428285, June 1990.
51. Vahdatj N, Delaney R "Decontamination of Chemical Protective Clothing" *Am Ind Hyg Assoc J* 50(3) 152-156, 1989

52. Williams L "Extent and Causes of Occupational Dermatitis in Painters and Maintenance Fitters"
1991 National Research Workshop on Occupational Skin Disorders and Occupational Cancer"
Worksafe Australia, Sydney, July 1991
53. Wu W, Prahinski J R "Some Theoretical Results of Swelling in Fiber or Particle Filled Polymers"
Polymer Engineering and Science 29(4) 268-272, 1989
54. Zellers E T, Sulewski R "Modelling the Temperature Dependence of N-Methypyrrolidone
Permeation Through Butyl - and Natural - Rubber Gloves" Am Ind Hyg Ass J 54(9) 465- 479,
1993

15. APPENDICES

15.1. Appendix A: Initial Report to Worksafe

Not included in this version

15.2. Appendix B: Reports for Safework

Not included in this version

15.3. Appendix C: Ethics and Workplace Agreement

WORKSAFE AUSTRALIA: GUIDELINES ON ETHICAL ASPECTS OF UNDERTAKING OCCUPATIONAL HEALTH AND SAFETY RESEARCH IN THE WORKPLACE USING HUMAN DATA

The broad principles of ethics in research apply to research carried out in occupational settings. This paper addresses issues that bear particular comment in workplace based research and should be read in conjunction with the National Health and Medical Research Council research guidelines (see attached NH&MRC guidelines).

These guidelines have been developed to facilitate the conduct of workplace research.

Health-related occupational research is conducted in a population bound by a contract of employment. This contractual relationship, which imposes common law and statutory obligation upon both employers and employees will influence ethical issues and the way in which research is conducted. Notably, primary control and an overriding duty of care remain with the employer.

Given the potential for conflicting interests and opinions between management and unions or employee representatives, and the fact that the livelihood of participating employees may depend upon the researcher's due regard to confidentiality and related ethical considerations, an informed and sensitive approach is essential. It is desirable that a co-operative frame work be established early in any project by involvement of relevant parties.

A research proposal may arise from within the industry (management or unions) or from an external agency. The relationship between employers, unions and researchers is critical to the success of the project, and the following guidelines should be followed:

1. Ethics Committee
Proposals for all research on human beings must be assessed by an appropriate independent ethics committee, regardless of whether or not invasive techniques are employed.
2. Advisory Committee
A formal consultative mechanism, for the period of the Research, such as an Advisory Committee, with membership to include representatives of employers, unions and researchers must be established before the research commences. Terms of reference should be agreed to and a mechanism for resolving differences determined.
3. Workplace Agreements
In the case of external agencies proposing research on employees, the employer and unions, at an appropriate level, should be approached for co-operation including signed workplace agreements. This co-operation should be sought as early as possible in the development of the research proposal. In the event of refusal, the external agency should refer the matter to an independent ethics committee and only consider studying subjects independently of a workplace agreement, if the Ethics Committee finds that this is appropriate.
4. Ownership of the Data
The ownership of the data, with the attendant rights and responsibilities, must be clearly established. Whilst exceptions will occur, it is recommended that such ownership normally be

vested in the research team. Agreement needs to be reached on measures for ensuring compliance with the principles of confidentiality (with particular regard to privacy of data concerning an individual's health status and/or work performance) and on the right to publish the results of the study in the scientific literature.

5. Feedback to Subjects

A system must be established by which the subjects, and other relevant parties, will be informed of the overall grouped results and their implications.

6. Informing Relevant Parties

Employers, employees and unions must be informed of all research questions being investigated, also the methods to be used, limitations in analysis and interpretation, and have group results given to them in readily understandable terms. Such information should be appropriately disseminated to workers via meetings, handouts and notice-boards. Any concerns of employers, unions or individuals, about aspects of the study need to be fully and frankly discussed.

7. Informing Subjects

At all times individuals will be informed of their own results, and this will involve an interpretation of those results in readily understandable terms.

8. Confidentiality

At no time will results which can be identified as belonging to an individual be given to the employer or another party, including the Advisory Committee, without written consent from the subject. This applies in all cases except where health surveillance and/or biological monitoring has been performed under the provision of the National Model Regulations to Control Hazardous Substances or other regulations, where normal provisions for employer access to information will apply.

9. Counselling Subjects

Where an individual's results indicate a significant abnormality, that person should be counselled about the implications of the results and a letter written for them to give to their personal physician.

10. Voluntary Participation

Participation in any research study will be at all times voluntary. Informed written consent shall be obtained from all individuals involved in experimental procedures, prior to any procedures taking place.

11. Freedom to Withdraw Participation

Individuals shall remain free to withdraw from participation at any stage of the study, without penalty or undue pressure.

12. Pre-existing Data

While the principle of informed consent generally applies, in some instances, for example where there is a body of existing data or where the data applies to deceased individuals, then the researcher will need to seek the advice of an independent Ethics Committee before obtaining access to that information.

13. Identification of Costs to Industry

The costs, both direct and indirect, of a research project that are to be borne by industry need to be identified and agreed.

14. Compensation to Subjects

The responsibility for compensation to any subject injured by invasive procedures or other procedures associated with the study should be clearly determined prior to data collection.

NHMRC STATEMENT ON HUMAN EXPERIMENTATION

To be read in conjunction with the supplementary notes

The collection of data from planned experimentation on human beings is necessary for the improvement of human health. Experiments range from those undertaken as a part of patient care to those undertaken either on patients or on healthy subjects for the purpose of contributing to knowledge, and include investigations on human behaviour. Investigators have ethical and legal responsibilities toward their subjects and should therefore observe the following principles:

1. The research must conform to generally accepted moral and scientific principles. To this end institutions in which human experimentation is undertaken should have a committee concerned with ethical aspects and all projects involving human experimentation should be submitted for approval by such a committee (see supplementary note 1 on institutional ethics committees).
2. Protocols of proposed projects should contain a statement by the investigator of the ethical considerations involved.
3. The investigator after careful consideration and appropriate consultation must be satisfied that the possible advantage to be gained from the work justifies any discomfort or risks involved.
4. The research protocol should demonstrate knowledge of the relevant literature and wherever possible be based on prior laboratory and animal experiments .
5. In the conduct of research, the investigator must at all times respect the personality, rights, wishes, beliefs, consent and freedom of the individual subject.
6. Research should be conducted only by suitably qualified persons with appropriate competence, having facilities for the proper conduct of the work; clinical research requires not only clinical competence but also facilities for dealing with any contingencies that may arise.
7. New therapeutic or experimental procedures which are at the stage of early evaluation and which may have long-term effects should not be undertaken unless appropriate provision has been made for long-term care, observation and maintenance of records.
8. Before research is undertaken the free consent of the subject should be obtained. To this end the investigator is responsible for providing the subject at his or her level of comprehension with sufficient information about the purpose, methods, demands, risks, inconveniences and discomforts of the study. Consent should be obtained in writing unless there are good reasons to the contrary. If consent is not obtained in writing, the circumstances under which it is obtained should be recorded.
9. The subject must be free at any time to withdraw consent to further participation.
10. Special care must be taken in relation to consent, and to safeguarding individual rights and welfare where the research involves children, the mentally ill and those in dependant relationships or comparable situations (see supplementary note 2 on research on children, the mentally ill and those in dependant relationships or comparable situations, including unconscious patients).
11. The investigator must stop or modify the research program or experiment if it becomes apparent during the course of it that continuation may be harmful.
12. Subject to maintenance of confidentiality in respect of individual patients, all members of research groups should be fully informed about projects on which they are working.
13. Volunteers -may be paid for inconvenience and time spent, but such payment should not be so large as to be an inducement to participate.

Notes:

1. (a) An application to the NH&MRC for a research grant involving human experimentation is required to be certified by the ethics committee of the applicant's institution as complying with the *NHMRC Statement on Human Experimentation and Supplementary Notes* before the application will be considered for funding.

- (b) Persons undertaking, human experimentation who are not associated with an institution should ensure that comments on their protocols are sought from an established ethics committee e.g. in a university or hospital.

15.3.1. Workplace Agreement

Dear

"Workplace Agreement" for Research Project

I have been invited to apply for a research grant from Worksafe Australia, following a successful review of a "expression of interest" some months ago. Nationally, about \$1,000,000 on research will be funded and about \$4,000,000 of research has been invited to apply. This gives this project about a 25% chance of success.

The topic of my project is "Use of Gloves to Control Chemical Exposure in the Workplace". I have noticed that all the information on gloves relates to new gloves with a very small amount of manufacturer's data on resistance to mixtures of chemicals. I propose to test gloves once they have been used in the workplace and also to see how much their chemical resistance varies over the surface of the glove. I have teamed up with a chemical engineer Dr Jimmy Yu who has extensive experience in sorbent beds and we think we can better understand how chemicals penetrate gloves. Appearance of gloves is not necessarily a good guide to replacement.

The outcome of this research is to produce better guidelines on how chemical gloves should be used in the workplace. This will include guidance on how long gloves actually give protection, and more technical advice on the way that they eventually fail. It is proposed to perform the work over the calendar year 1994.

This information should be of real use to both employers and employees.

Part of the requirements to be considered for funding, is to work out ground rules for doing the research. Worksafe Australia has produced guidelines (attached), which details what should be considered in developing a "Workplace Agreement" -see point 3. This effectually means a free flow of information to interested parties, appropriate confidentiality and external vetting by an ethics committee. I see the main ethical issue as the responsibility of the researchers (myself) to inform without delay the employees and employer if the results are untoward.

I have drafted a "Workplace Agreement" which I would like you to consider. Unfortunately, I have left this aspect of the preparation of the research proposal until today, and the agreed Workplace Agreements have to be in Sydney with my proposal by **July 30**.

Yours sincerely

Workplace Agreement

The undersigned have read the Worksafe Australia Guidelines and the attached NHMRC Statement. I agree to cooperate with the research project "Use of Gloves to Control Chemical Exposure in the Workplace" if it is funded by Worksafe Australia. In particular:

1. Agree to representation on an "Advisory Committee" per section 2.
2. Agree that ownership of the data is with the researchers, but that they will freely share the information (section 3, 5, 6, 7) whilst respecting the confidences per section 8.
3. If a test result or set of test results indicate something untoward, then without delay, the employee(s) wearing the glove(s) and employer shall be informed and if appropriate, the employee counselled (section 9).
4. Participation in this project will be voluntary (section 10, 11), though it is recognised that ownership of the gloves will normally be either with the employer or researcher. There should be no direct contact with the employee, other than observation of the use of gloves. All participants (wearers of gloves) will be informed in writing of the project before it begins.
5. No pre-existing data is known to exist (section 12)
6. Costs to industry, direct and indirect, will be identified and agreed before the project starts. The project has budgeted \$700 for gloves. At \$6 a pair, this equates to 116 pairs. It is expected that only gloves that are not used for their normal life project will be bought by the project. The time costs of involvement in the project are expected to be minimal, outside those involved in the "Advisory Committee" (section 2) and discussions on the running of the project. Where possible, the meetings will be at the workplace, to minimise inconvenience to the employer. All interested parties will be free to visit the laboratory to view the testing apparatus.
7. There should be no need to compensate the wearers of the gloves (section 14) as the testing is not invasive.

Agreed

Date July th 1993

15.4. Appendix D: Hardware

Table 35 Suppliers of Parts

ITEM DESCRIPTION	ITEM SOURCE
Quick Connectors 5mm to 6mm tubing QSM-M5-6 1/8 BSP to 6mm tubing QS-1/8-6	Festo 42 Turbo Drive Cooparoo Queensland 4151 Ph (07) 391 6933 Fax (07) 391 5546
Quick Connectors (PARKER) 1/8 BSP to 6mm tubing	Air and Hydraulic Industries Pty Ltd 2/286 Evans Rd Salisbury Queensland 4107 Ph (07) 277 6255 Fax (07) 277 6129
Flow Metering Valves & Fittings NUPRO S Series Fine Metering Valve Part No. B SS4 1/4" Swagelok	Brisbane Valve and Fitting 60 Commercial Road Newstead Queensland 4006 Ph (07) 252 8900 Fax (07) 264 6842
Solenoid Pneumatic Valves MFH-3-M5 Single BMFH-2-3-M5 Double MSFG-12 Coil	Festo 42 Turbo Drive Cooparoo Queensland 4151 Ph (07) 391 6933 Fax (07) 391 5546
Programmable Logic Controller PC-IO-XX Series	ProCon Technology PO Box 655 Mt Waverley 3149 Ph (03) Fax (03) 807 8220
A to D and D to A	ProCon Technology PO Box 655 Mt Waverley 3149 Ph (03) Fax (03) 807 8220
Flow Distributing Manifolds	Designed in house and manufactured by the Environmental Science Workshop Griffith University Nathan
High Purity Nitrogen	CIG Industrial Gases
Computer 486 SX-33 (Intel) 4Mb Ram Vesa Local Bus	Concord Computers PO Box 6147 Upper Mt Gravatt 4122 Ph (07) 343 8555 Fax (07) 343 8449
Flow meter AMW 3300 Microbridge mass airflow sensor/amplifier	Honeywell Limited Industrial Automation & Control Division 213 Riverside Drive West End Queensland 4101 Ph (07) 840 6479 Fax (07) 840 6469
ASTM Cell	Labglass Pty Ltd PO Box 1173 Stafford Queensland 4053 Ph (07) 356 8199 Fax (07)356 6722
Glove Test Cells Small, large and Intermittent	Designed in house and manufactured by the Environmental Science Workshop Griffith University Nathan
Tubing 6mm OD Nylon 2000 KPa Burst Pressure	Tony Powell Hose Supply 776 Beaudesert Rd Salisbury Queensland 4107 Ph (07) 274 1480 Fax (07) 274 2967
<i>GloveTest</i> Software	Designed in House with Microsoft Visual Basic Version 3.0, Professional Edition.

15.5. Appendix E: National Safety Council Guidelines

This appendix is reproduced from Hassler (Hassler 1989)

“These guidelines for glove selection appeared in the June 1988 issue of **Safety and Health** which is published by the National Safety Council. This is the only published list of official rules which guide selection and use of gloves.”

National Safety Council Guidelines

Preliminary Information Before Glove Selection

1. Review processes, work practices and engineering controls for ways to eliminate the need for gloves. Glove controls for ways to eliminate the need for gloves. Glove use should be the last approach considered to provide employees with protection against skin contact with chemicals.
2. List all the chemicals against which protection is sought and estimate the wearing time requirement for gloves (e.g. all day, few hours, periodically for minutes).
3. Determine from MSDS and other sources the known consequences of skin contact with chemicals to be used (e.g. sensitisation, dermatitis, systemic poisoning, skin absorbable).
4. Single Agents. Find the chemical against which skin contact protection is sought from among those listed in various sources of permeation data (see manufacturer's published literature e.g. Edmont, North, Dow, DuPont, Pioneer, AIHA Monograph). Choose gloves which provide the best performance based on breakthrough time.
5. Mixtures. For protection against chemical mixtures where component permeability data exist and components are known not be skin absorbable, systemic poisons, corrosives or sensitisers, select gloves which maximise protection against the component(s) likely to be present in greatest quantity (see Appendix Note 1).
6. Gloves should not be selected for protection against mixtures based on component permeability data if a mixture component is skin absorbable, a systemic poison, corrosive or sensitiser.

Glove Selection: Permeability Data not available.

7. When protection is sought against single agents or mixture component for which there is consistent toxicological evidence of high systemic toxicity, skin absorbability or irreversible effects, experimental determination of chemical permeability through gloves should be made. Gloves selected should have at least a 30 minute breakthrough time.
8. When seeking protection against chemicals for which toxicological evidence suggests a less serious hazard and there are no permeability data available, use the following selection procedure:
9. Use any two glove pairs of different composition from the permeation guide and treat the outer glove as disposable and discard it frequently, or
10. Use any single glove as disposable to be discarded after completing the operation for which protection was needed or 15 minutes, whichever is sooner.

Other Selection Factors

11. After selection of gloves based on permeability data, or after selecting suitable double glove system, the following additional factors should be considered. Durability; dexterity; tactile sensitivity; friction; wearing schedule (all day, short term/frequent); cost.
12. Gloves chosen based on best permeability may not always be the best for other selection factors, but should reflect a best effort to optimise factors which are often at cross purposes (e.g. glove thickness favours reduced permeability and improved durability, but may compromise dexterity and touch).

Glove Use

13. Gloves are not intended to permit contact with chemicals, but are intended to prevent contact when accidental encounter occur. Gloves should be kept as clean as possible during use.
14. Gloves should only be used as protection against the agent considered during the selection process. Do not use gloves work to protect skin from chemicals to clean-up broken glass or to handle unusually hot or cold objects. Gloves in contact with chemicals substantially above ambient temperatures may not provide the protection predicted by permeability data developed at another temperature.
15. The loss of tactile sensitivity during glove use may result in glove contamination without the wearer's knowledge. This increase the risk of (1) area contamination and (2) personal exposure and enhanced health effects.
16. Minimise the spread of contamination throughout the work area and beyond by making the location where gloves are to be used clearly known to all area personnel.
17. Rinse gloves frequently to minimise the spread of contamination within a designated glove-use area or to the face and mouth of the wearer. Frequent rinsing will also eliminate continued chemical challenge to gloves contaminated without the wearer's knowledge. Rinsing is recommended every half-hour and after high-potential contact operations. Even well-selected gloves will fail with continued chemical contact. The consequences could be patching of a permeated chemical on the skin and enhanced skin or systemic effects.

Glove Reuse, Disposal and Storage

18. When evidence of glove contact with chemicals other than those known to be skin absorbable, systemic poisons, or corrosives or sensitisers is visible or otherwise known or suspected, the contaminant(s) may be washed from the glove and the glove continued in service or reused.
19. When evidence of glove contact with chemicals known to be skin absorbable, systemic poisons, corrosives or skin sensitisers, is visible, otherwise known or suspected the glove should be discarded (see Appendix Note 2).
20. Do not reuse gloves at the end of the work-week unless chemical contact is known not to have occurred.
21. If gloves are washed or otherwise cleaned with a specialised decontamination solution before disposal, contain any washings not permitted in the sewers.
22. Gloves removed for disposal need not be decontaminated. In general one contaminated glove should be peeled or stripped almost entirely off by turning the glove inside-out. Before removing it completely, use the partially removed glove as protection while similarly removing the second glove. A container should be ready to receive contaminated gloves for proper water disposal.
23. Before reusing gloves, (1) wash the outside with soap and water, (2) remove the glove from the hand without mechanically stressing the glove, (3) rinse the glove inside and out, (4) dry the glove thoroughly and store it in a clean place. The washing procedure should not be used for water soluble gloves (e.g. PVA).
24. Gloves known or assumed to be contaminated to the extent that their washings would not be permitted in the sewer should be discarded in accordance with proper disposal procedures.
25. Washing gloves with solvent (e.g. acetone) may have unpredictable effects on the elastomer's ability to protect when gloves are reused, so reuse of solvent washed gloves is not recommended.

Note 1 - Protection against mixtures

The limitation discussed below concerns direct application of single agent permeability data on mixtures of these chemicals. Research indicated that for mixtures which show no component adverse synergism towards glove material (mixture permeability no worse than predicted component permeability) the permeation rate of these mixtures will be directly proportional to volumetric concentration of each solvent. This behaviour cannot be predicted without conducting permeability studies but may be assumed without serious consequences for less hazardous chemicals. For protection against mixtures which do not contain hazardous chemicals you may select gloves which maximise protection against the component present in greatest concentration.

When protection is required against mixtures containing at least one of the hazardous materials (skin absorbable, systemic poison, corrosive or sensitiser), it is not reasonable to assume that there are no component adverse synergistic effects making mixtures more permeable than expected based on known component permeability. In this case a glove should not be selected until the permeability of the mixture has been determined experimentally and found acceptable.

Note 2 - Effect of Glove Washing

Most glove permeability data has been developed for single agents in continuous contact with glove material. When a glove is contaminated and then washed, some of the chemical which began to permeate the glove will continue toward and may reach the hand. For less hazardous chemicals continued use of a contaminated but washed glove is not expected to pose a serious hazard. For materials known to be skin or systemically hazardous continued use of a contaminated but washed glove could pose a more serious hazard and is not recommended.

As stated in paragraphs 15 and 16, frequent rinsing of gloves worn for extended periods will minimise area contamination, glove permeation, and skin contact resulting from glove contamination which occurs without the workers' knowledge. This work practice is strongly recommended because (1) area contamination e.g. workbench, equipment, desk, telephone etc.) can have serious consequences to the unprotected worker who is exposed later and (2) chemical breakthrough while the glove is in long term use can lead to enhanced absorption and a more serious health problem than the same exposure to even the ungloved hand (patch effect).

15.6. Appendix F: Laboratory Trials Data

Not included in this version

(Data was presented in an electronic form on the attached disk. in a subdirectory DATA.)

15.7. Appendix G: Pilot Trials Data

Data from Pilot Trials on new and used gloves to investigate the degree of variation between new and used gloves. An incidental, but surprisingly relevant classification of the samples was the noting of **position** per the table below.

Table 36 Codes for Glove Position and Glove Type



Position	Front	Back
Fingers	1	1.5
Top Palm	2	2.5
Mid Palm	3	3.5
Heel of Palm	4	4.5
Gauntlet	5	5.5

Glove Type	Project Code
1	MSA PVC (Australian made)
1A	Metalguard
1B	Solvguard
2	Ansell
2A	Singe Dipped PVC
2B	Double Dipped PVC
2C	Other

The data below shows the form of the data recorded in files on the computer. In this form, the indices which have been calculated mathematically by the *GloveTest* program are recorded, rather than the raw data. The raw data from the *GloveTest* rig is recorded in the file in the first column.

Table 37 New Ansell double dipped PVC (type 2B)

Filename	Run	Cell	Position	New	Type	Solvent	Midpoint T	Midpoint v	Slope	Intercept	BT	MaxV	MaxT	TopSlop e	TopInterc ept	SSPR	LT	Integral2 0	Integral3 0
AN_A1.GLV	A	1	1.0	New	2B	1	517	1,077	4	(759)	214	3,636	2,691	(0)	4,024	58	545	35,940	71,560
AN_A2.GLV	A	2	1.0	New	2B	1	512	508	3	(817)	316	3,521	2,927	(0)	3,876	57	780	25,877	58,471
AN_A3.GLV	A	3	1.0	New	2B	1	509	542	3	(784)	301	3,649	2,804	(0)	3,990	59	747	26,728	61,362
AN_A4.GLV	A	4	1.0	New	2B	1	506	304	2	(730)	357	3,541	3,042	(0)	3,834	58	882	21,346	53,362
AN_A5.GLV	A	5	1.0	New	2B	1	498	898	3	(832)	239	3,659	2,792	(0)	3,887	60	624	33,879	69,956
AN_A6.GLV	A	6	1.0	New	2B	1	496	715	3	(758)	255	3,661	2,791	(0)	3,772	60	715	29,951	65,501
AN_A7.GLV	A	7	1.0	New	2B	1	493	545	2	(537)	245	3,329	2,908	(0)	3,554	54	777	23,568	54,486
AN_A8.GLV	A	8	1.0	New	2B	1	490	634	3	(700)	257	3,600	2,785	(0)	3,888	58	702	27,572	61,308
AN_E1.GLV	E	1	1.0	New	2B	1	2,441	757	1	(1,245)	1,518	2,375	9,429	(0)	2,695	16	2,597	236	1,166
AN_E2.GLV	E	2	1.0	New	2B	1	2,555	1,068	1	(1,119)	1,307	2,484	9,060	0	2,396	19	2,536	447	1,831
AN_E3.GLV	E	3	1.0	New	2B	1	2,547	787	1	(1,352)	1,610	2,385	9,416	(0)	2,423	16	2,652	107	746
AN_E4.GLV	E	4	1.0	New	2B	1	1,830	593	1	(1,835)	1,273	2,588	8,446	(0)	2,658	21	2,424	229	2,038
AN_E5.GLV	E	5	1.0	New	2B	1	1,947	1,020	1	(1,236)	1,067	2,726	8,323	0	2,659	24	2,302	655	3,745
AN_E6.GLV	E	6	1.0	New	2B	1	2,045	773	1	(1,258)	1,266	2,615	8,422	(0)	2,662	21	2,458	310	2,077
AN_E7.GLV	E	7	1.0	New	2B	1	2,630	834	1	(1,427)	1,660	2,356	9,381	0	2,313	16	2,639	257	1,207
AN_E8.GLV	E	8	1.0	New	2B	1	1,911	697	1	(1,459)	1,294	2,622	8,408	(0)	3,057	22	2,421	398	2,621
AN_F1.GLV	F	1	1.0	New	2B	1	3,135	932	1	(1,720)	2,033	2,354	9,177	(0)	2,410	19	2,819	207	516
AN_F3.GLV	F	3	1.0	New	2B	1	2,287	969	1	(1,489)	1,385	2,609	8,559	(0)	3,184	28	2,538	360	1,819
AN_F4.GLV	F	4	1.0	New	2B	1	2,166	944	1	(1,234)	1,228	2,548	8,558	(0)	2,807	27	2,485	305	2,092
AN_F5.GLV	F	5	1.0	New	2B	1	2,280	1,115	1	(1,280)	1,218	2,626	8,552	(0)	3,302	28	2,474	314	2,105
AN_F6.GLV	F	6	1.0	New	2B	1	2,518	804	1	(1,109)	1,460	2,344	8,915	0	2,328	21	2,610	310	1,314
AN_F7.GLV	F	7	1.0	New	2B	1	3,115	1,042	1	(1,242)	1,694	2,243	8,914	(0)	2,498	19	2,716	219	845
AN_F8.GLV	F	8	1.0	New	2B	1	3,113	1,165	1	(1,163)	1,555	2,466	9,278	(0)	2,589	20	2,680	249	1,079
AN_G1.GLV	G	1	1.5	New	2B	1	2,303	1,070	1	(1,682)	1,407	2,500	6,376	0	2,503	18	2,258	155	1,555
AN_G2.GLV	G	2	1.5	New	2B	1	2,061	905	1	(1,594)	1,315	2,561	8,061	(0)	2,853	19	2,180	434	2,339
AN_G3.GLV	G	3	1.5	New	2B	1	1,582	786	1	(1,445)	1,025	2,919	5,649	(0)	3,107	22	1,955	808	4,780
AN_G5.GLV	G	5	1.5	New	2B	1	1,446	478	1	(1,124)	1,015	2,658	7,077	(0)	3,065	19	2,003	549	3,725
AN_G6.GLV	G	6	1.5	New	2B	1	2,631	834	1	(1,509)	1,695	2,292	8,881	(0)	2,473	13	2,474	113	957
AN_G7.GLV	G	7	1.5	New	2B	1	1,676	437	1	(1,090)	1,196	2,484	8,276	(0)	2,805	17	2,184	412	2,652
AN_G8.GLV	G	8	1.5	New	2B	1	2,986	942	1	(1,162)	1,649	2,228	9,486	0	1,975	11	2,517	151	746
AN_H1.GLV	H	1	1.5	New	2B	1	2,288	919	1	(1,379)	1,373	2,509	8,909	(0)	2,715	16	2,276	329	1,667
AN_H2.GLV	H	2	1.5	New	2B	1	2,763	636	1	(1,148)	1,778	2,259	9,760	0	1,950	10	2,561	199	501
AN_H3.GLV	H	3	1.5	New	2B	1	1,688	918	1	(1,247)	972	2,835	8,300	(0)	3,078	21	1,927	1,009	4,865
AN_H4.GLV	H	4	1.5	New	2B	1	2,880	973	1	(1,041)	1,488	2,299	9,637	(0)	2,389	12	2,421	167	844
AN_M1.GLV	M	1	2.5	New	2B	1	2,173	784	1	(1,480)	1,420	2,721	8,065	(0)	2,866	19	2,447	326	1,612
AN_M2.GLV	M	2	2.5	New	2B	1	1,090	1,113	3	(1,789)	672	3,556	3,719	(0)	3,741	33	1,523	4,541	16,582
AN_M3.GLV	M	3	2.5	New	2B	1	1,206	923	2	(1,584)	762	3,321	4,076	(0)	3,517	30	1,694	2,977	11,791
AN_M4.GLV	M	4	2.5	New	2B	1	490	282	1	(370)	278	3,563	3,715	(0)	3,720	33	1,388	7,692	20,647
AN_M5.GLV	M	5	2.5	New	2B	1	489	414	2	(537)	276	3,653	3,235	(0)	3,815	33	1,191	10,566	25,931
AN_M6.GLV	M	6	2.5	New	2B	1	1,439	1,158	2	(1,667)	849	3,291	4,431	(0)	3,383	30	1,823	2,237	11,374
AN_M7.GLV	M	7	2.5	New	2B	1	1,199	1,376	3	(1,647)	653	3,614	3,830	(0)	3,814	33	1,559	6,199	18,746
AN_M8.GLV	M	8	2.5	New	2B	1	1,318	1,317	2	(1,865)	773	3,472	4,069	(0)	3,665	32	1,681	4,339	15,123
AN_I1.GLV	I	1	3.0	New	2B	1	1,465	1,140	2	(1,264)	770	2,988	4,458	(0)	3,125	34	1,902	4,086	10,855
AN_I2.GLV	I	2	3.0	New	2B	1	1,940	1,221	1	(1,482)	1,064	2,664	4,938	(0)	2,938	29	2,148	1,593	5,141
AN_I3.GLV	I	3	3.0	New	2B	1	1,696	1,193	2	(1,531)	953	2,874	4,813	0	2,755	32	2,052	1,970	7,009
AN_I5.GLV	I	5	3.0	New	2B	1	1,802	1,326	2	(1,708)	1,015	2,959	5,041	(0)	3,652	32	2,072	1,557	6,150
AN_I6.GLV	I	6	3.0	New	2B	1	1,681	1,302	2	(1,514)	904	2,903	4,678	(0)	3,117	33	2,009	1,772	7,255
AN_I7.GLV	I	7	3.0	New	2B	1	1,678	912	1	(1,324)	994	2,432	4,916	(0)	2,574	27	2,084	1,395	6,428
AN_K1.GLV	K	1	3.5	New	2B	1	1,577	1,086	2	(1,409)	890	2,691	4,702	(0)	2,731	40	2,154	2,047	7,448
AN_K2.GLV	K	2	3.5	New	2B	1	2,050	905	1	(1,571)	1,301	2,623	8,206	(0)	2,875	34	2,447	556	2,512
AN_K3.GLV	K	3	3.5	New	2B	1	1,689	976	1	(1,491)	1,021	2,681	5,177	0	2,645	38	2,242	1,219	5,240
AN_K4.GLV	K	4	3.5	New	2B	1	1,449	1,176	2	(1,663)	849	3,099	4,331	(0)	3,281	46	2,077	2,476	9,569
AN_K5.GLV	K	5	3.5	New	2B	1	1,564	1,135	2	(1,273)	827	2,846	4,689	0	2,847	42	2,138	2,348	8,031
AN_K6.GLV	K	6	3.5	New	2B	1	1,682	843	1	(1,258)	1,007	2,698	6,379	(0)	2,813	36	2,295	1,143	4,652
AN_K7.GLV	K	7	3.5	New	2B	1	1,561	1,108	2	(1,410)	874	2,766	4,687	(0)	2,779	40	2,134	1,730	7,266
AN_L1.GLV	L	1	4.5	New	2B	1	1,240	1,049	2	(1,611)	751	3,114	3,893	(0)	3,362	51	1,515	3,990	22,443
AN_L2.GLV	L	2	4.5	New	2B	1	1,596	1,154	2	(1,681)	946	3,054	4,857	(0)	3,310	49	1,800	1,775	13,364
AN_L3.GLV	L	3	4.5	New	2B	1	1,226	1,099	2	(1,928)	781	3,307	3,879	0	3,361	55	1,486	3,815	24,202
AN_L4.GLV	L	4	4.5	New	2B	1	1,345	967	2	(1,888)	889	3,107	4,241	0	3,109	51	1,643	2,185	17,375
AN_L5.GLV	L	5	4.5	New	2B	1	1,217	1,075	2	(1,761)	756	3,321	3,991	(0)	3,516	55	1,510	3,763	23,202
AN_L6.GLV	L	6	4.5	New	2B	1	1,336	1,124	2	(1,669)	798	3,068	4,111	(0)	3,230	50	1,572	2,865	19,171
AN_L7.GLV	L	7	4.5	New	2B	1	969	944	2	(1,473)	591	3,519	3,500	(0)	3,817	58	1,314	6,794	31,676
AN_L8.GLV	L	8	4.5	New	2B	1	1,447	1,209	2	(1,646)	834	3,154	4,343	(0)	3,385	52	1,657	2,654	17,202
AN_C1.GLV	C	1	5.5	New	2B	1	531	679	3	(960)	311	3,655	2,812	(0)	3,885	60	1,154	18,439	47,108
AN_C2.GLV	C	2	5.5	New	2B	1	523	2,035	5	(359)	78	3,655	2,684	(0)	3,655	60	1,004	28,243	57,468
AN_C3.GLV	C	3	5.5	New	2B	1	519	446	2	(790)	332	3,568	2,920	(0)	3,919	57	1,189	14,971	41,661
AN_C4.GLV	C	4	5.5	New	2B	1	515	746	3	(905)	282	3,655	2,797	(0)	3,676	61	1,152	19,210	48,264
AN_C5.GLV	C	5	5.5	New	2B	1	499	603	3	(867)	294	3,655	2,780	(0)	4,016	59	1,121	17,491	45,731
AN_C6.GLV	C	6	5.5	New	2B	1	497	735	3	(756)	252	3,652	2,779	(0)	3,671	61	1,142	18,702	47,737
AN_C7.GLV	C	7	5.5	New	2B	1	496	709	3	(917)	280	3,614	2,657	(0)	4,059	57	1,044	18,990	47,577
AN_C8.GLV	C	8	5.5	New	2B	1	487	579	3	(851)	290	3,653	2,768	(0)	3,763	60	1,145	17,576	46,375
AN_D2.GLV	D	2	5.5	New	2B	1	505	510	3	(819)	311	3,591	2,913	(0)	3,725	59	877	24,175	55,023
AN_D3.GLV	D	3	5.5	New	2B	1	504	354	2	(616)									

For a limited number of indices, the confidence intervals have been calculated in the table below.

Table 38 Confidence Intervals - New Ansell PVC double dipped gloves

Statistic	Position	MidpointT	Midpointv	Slope	Intercept	BT	MaxV	MaxT	TopSlope	TopIntercept	SSPR	LT	Integral20	Integral30
Count	1.0	23	23	23	23	23	23	23	23	23	23	23	23	23
Std Dev	1.0	1002.5	225.1	0.9540	311.4	600.8	544.1	2947.3	0.0485	633.3	18.11	901.9	13823.9	29622.6
Confidence	1.0	409.7	92.0	0.3899	127.3	245.6	222.4	1204.5	0.0198	258.8	7.40	368.6	5649.5	12106.2
UCL	1.0	3115.6	1536.1	2.7483	-2353.9	1819.9	5511.3	12324.0	-0.1135	5898.1	60.39	3468.0	14303.9	33216.1
LCL	1.0	1353.0	722.0	1.1792	-1240.6	787.2	2644.5	5559.8	-0.0667	2819.6	26.50	1549.7	4327.2	10554.9
Mean	1.0	1762.7	814.0	1.5691	-1113.3	1032.7	2866.8	6764.3	-0.0468	3078.5	33.90	1918.3	9976.7	22661.1
Count	1.5	11	11	11	11	11	11	11	11	11	11	11	11	11
Std Dev	1.5	557.4	206.3	0.2581	221.3	282.7	230.7	1350.8	0.0282	411.8	4.13	225.7	293.9	1592.9
Confidence	1.5	329.4	121.9	0.1525	130.8	167.1	136.3	798.2	0.0167	243.4	2.44	133.4	173.7	941.3
UCL	1.5	2538.8	931.0	1.1583	-1180.2	1522.7	2640.3	9017.5	-0.0008	2871.9	18.62	2383.9	566.9	3180.5
LCL	1.5	1880.1	687.1	0.8533	-1441.7	1188.6	2367.7	7421.0	-0.0341	2385.2	13.74	2117.1	219.5	1297.8
Mean	1.5	2209.5	809.0	1.0058	-1311.0	1355.6	2504.0	8219.3	-0.0174	2628.5	16.18	2250.5	393.2	2239.2
Count	2.5	23	23	23	23	23	23	23	23	23	23	23	23	23
Std Dev	2.5	510.3	183.0	0.2068	194.2	270.3	193.2	989.2	0.0282	365.1	4.97	239.0	217.6	1263.5
Confidence	2.5	208.5	74.8	0.0845	79.4	110.5	78.9	404.3	0.0115	149.2	2.03	97.7	88.9	516.4
UCL	2.5	4454.4	1662.4	1.8688	-2733.1	2688.9	4944.8	16549.1	-0.0527	5206.3	36.47	4714.7	627.2	3454.2
LCL	2.5	2122.9	793.8	0.8921	-1406.2	1289.2	2432.9	8072.4	-0.0321	2528.6	17.22	2308.5	269.2	1468.9
Mean	2.5	2331.5	868.6	0.9767	-1326.9	1399.7	2511.9	8476.7	-0.0206	2677.8	19.25	2406.2	358.1	1985.3
Count	3.0	6	6	6	6	6	6	6	6	6	6	6	6	6
Std Dev	3.0	157.1	149.4	0.1529	158.8	103.4	214.9	210.8	0.0542	372.9	2.55	83.3	1011.0	1965.4
Confidence	3.0	125.7	119.5	0.1223	127.1	82.7	171.9	168.7	0.0433	298.4	2.04	66.6	808.9	1572.6
UCL	3.0	1885.1	1310.2	1.6605	-1384.9	1068.6	2938.4	5045.9	-0.0045	3305.7	32.92	2139.8	2466.3	7969.1
LCL	3.0	1633.7	1071.1	1.4159	-1639.1	903.1	2594.5	4708.5	-0.0912	2708.9	28.83	2006.6	848.4	4823.8
Mean	3.0	1759.4	1190.6	1.5382	-1512.0	985.9	2766.4	4877.2	-0.0479	3007.3	30.88	2073.2	1657.4	6396.4
Count	3.5	7	7	7	7	7	7	7	7	7	7	7	7	7
Std Dev	3.5	193.0	126.1	0.2518	148.4	165.4	160.6	1384.8	0.0184	203.6	3.92	126.5	704.0	2382.7
Confidence	3.5	143.0	93.4	0.1865	109.9	122.5	118.9	1025.9	0.0136	150.8	2.91	93.7	521.5	1765.1
UCL	3.5	1796.1	1126.0	1.7024	-1329.3	1089.5	2890.9	6478.9	0.0018	3003.9	42.21	2306.2	2167.2	8153.6
LCL	3.5	1510.2	939.2	1.3293	-1549.1	844.5	2653.0	4427.1	-0.0254	2702.2	36.40	2118.8	1124.1	4623.3
Mean	3.5	1653.1	1032.6	1.5159	-1439.2	967.0	2771.9	5453.0	-0.0118	2853.0	39.30	2212.5	1645.7	6388.5
Count	4.5	8	8	8	8	8	8	8	8	8	8	8	8	8
Std Dev	4.5	184.4	90.1	0.2457	148.7	106.1	162.4	399.2	0.0311	210.6	3.09	143.8	1561.9	5610.4
Confidence	4.5	127.8	62.4	0.1703	103.1	73.5	112.5	276.6	0.0215	145.9	2.14	99.6	1082.3	3887.7
UCL	4.5	1424.8	1140.1	2.3455	-1604.1	866.8	3318.1	4378.5	-0.0180	3532.2	54.84	1661.8	4562.4	24967.1
LCL	4.5	1169.2	1015.3	2.0050	-1810.3	719.8	3093.0	3825.2	-0.0610	3240.4	50.55	1462.6	2397.7	17191.6
Mean	4.5	1297.0	1077.7	2.1752	-1707.2	793.3	3205.6	4101.9	-0.0395	3386.3	52.70	1562.2	3480.1	21079.4
Count	5.5	15	15	15	15	15	15	15	15	15	15	15	15	15
Std Dev	5.5	121.1	432.7	0.6523	176.5	83.1	153.3	203.4	0.0546	178.4	2.64	191.5	6670.7	9101.1
Confidence	5.5	61.3	219.0	0.3301	89.3	42.0	77.6	102.9	0.0276	90.3	1.34	96.9	3375.8	4605.7
UCL	5.5	596.0	1082.6	3.4563	-701.2	308.6	3670.7	2938.2	-0.0384	3875.8	60.05	1083.2	25854.3	56417.7
LCL	5.5	473.4	644.7	2.7961	-879.8	224.5	3515.6	2732.4	-0.0936	3695.2	57.38	889.4	19102.7	47206.3
Mean	5.5	534.7	863.7	3.1262	-790.5	266.5	3593.2	2835.3	-0.0660	3785.5	58.72	986.3	22478.5	51812.0

UCL 95 % upper confidence limit, LCL 95% lower confidence limit, Av Mean (average) value

The figures below are derived from the figures above, but only show data for the most interesting indices BT, LT, SSPR, INT20 and INT30. Arranged in this form they can be used to graph the effects of position on these indices, showing the mean value and the 95% confidence interval. Thus real trends can be eyeballed between back and front of a glove and along a glove.

Table 39 New Ansell PVC gloves - Effect of position on five indices

Statistic	Position	MidpointT	Midpointv	Slope	Intercept	BT	MaxV	MaxT	TopSlope	TopIntercep t	SSPR	LT	Intergral20	Intergral30
Count	1.0	23	23	23	23	23	23	23	23	23	23	23	23	23
Std Dev	1.0	1002.5	225.1	0.9540	311.4	600.8	544.1	2947.3	0.0485	633.3	18.11	901.9	13823.9	29622.6
Confidence	1.0	409.7	92.0	0.3899	127.3	245.6	222.4	1204.5	0.0198	258.8	7.40	368.6	5649.5	12106.2
UCL	1.0	3115.6	1536.1	2.7483	-2353.9	1819.9	5511.3	12324.0	-0.1135	5898.1	60.39	3468.0	14303.9	33216.1
LCL	1.0	1353.0	722.0	1.1792	-1240.6	787.2	2644.5	5559.8	-0.0667	2819.6	26.50	1549.7	4327.2	10554.9
Mean	1.0	1762.7	814.0	1.5691	-1113.3	1032.7	2866.8	6764.3	-0.0468	3078.5	33.90	1918.3	9976.7	22661.1
Count	1.5	11	11	11	11	11	11	11	11	11	11	11	11	11
Std Dev	1.5	557.4	206.3	0.2581	221.3	282.7	230.7	1350.8	0.0282	411.8	4.13	225.7	293.9	1592.9
Confidence	1.5	329.4	121.9	0.1525	130.8	167.1	136.3	798.2	0.0167	243.4	2.44	133.4	173.7	941.3
UCL	1.5	2538.8	931.0	1.1583	-1180.2	1522.7	2640.3	9017.5	-0.0008	2871.9	18.62	2383.9	566.9	3180.5
LCL	1.5	1880.1	687.1	0.8533	-1441.7	1188.6	2367.7	7421.0	-0.0341	2385.2	13.74	2117.1	219.5	1297.8
Mean	1.5	2209.5	809.0	1.0058	-1311.0	1355.6	2504.0	8219.3	-0.0174	2628.5	16.18	2250.5	393.2	2239.2
Count	2.5	23	23	23	23	23	23	23	23	23	23	23	23	23
Std Dev	2.5	510.3	183.0	0.2068	194.2	270.3	193.2	989.2	0.0282	365.1	4.97	239.0	217.6	1263.5
Confidence	2.5	208.5	74.8	0.0845	79.4	110.5	78.9	404.3	0.0115	149.2	2.03	97.7	88.9	516.4
UCL	2.5	4454.4	1662.4	1.8688	-2733.1	2688.9	4944.8	16549.1	-0.0527	5206.3	36.47	4714.7	627.2	3454.2
LCL	2.5	2122.9	793.8	0.8921	-1406.2	1289.2	2432.9	8072.4	-0.0321	2528.6	17.22	2308.5	269.2	1468.9
Mean	2.5	2331.5	868.6	0.9767	-1326.9	1399.7	2511.9	8476.7	-0.0206	2677.8	19.25	2406.2	358.1	1985.3
Count	3.0	6	6	6	6	6	6	6	6	6	6	6	6	6
Std Dev	3.0	157.1	149.4	0.1529	158.8	103.4	214.9	210.8	0.0542	372.9	2.55	83.3	1011.0	1965.4
Confidence	3.0	125.7	119.5	0.1223	127.1	82.7	171.9	168.7	0.0433	298.4	2.04	66.6	808.9	1572.6
UCL	3.0	1885.1	1310.2	1.6605	-1384.9	1068.6	2938.4	5045.9	-0.0045	3305.7	32.92	2139.8	2466.3	7969.1
LCL	3.0	1633.7	1071.1	1.4159	-1639.1	903.1	2594.5	4708.5	-0.0912	2708.9	28.83	2006.6	848.4	4823.8
Mean	3.0	1759.4	1190.6	1.5382	-1512.0	985.9	2766.4	4877.2	-0.0479	3007.3	30.88	2073.2	1657.4	6396.4
Count	3.5	7	7	7	7	7	7	7	7	7	7	7	7	7
Std Dev	3.5	193.0	126.1	0.2518	148.4	165.4	160.6	1384.8	0.0184	203.6	3.92	126.5	704.0	2382.7
Confidence	3.5	143.0	93.4	0.1865	109.9	122.5	118.9	1025.9	0.0136	150.8	2.91	93.7	521.5	1765.1
UCL	3.5	1796.1	1126.0	1.7024	-1329.3	1089.5	2890.9	6478.9	0.0018	3003.9	42.21	2306.2	2167.2	8153.6
LCL	3.5	1510.2	939.2	1.3293	-1549.1	844.5	2653.0	4427.1	-0.0254	2702.2	36.40	2118.8	1124.1	4623.3
Mean	3.5	1653.1	1032.6	1.5159	-1439.2	967.0	2771.9	5453.0	-0.0118	2853.0	39.30	2212.5	1645.7	6388.5
Count	4.5	8	8	8	8	8	8	8	8	8	8	8	8	8
Std Dev	4.5	184.4	90.1	0.2457	148.7	106.1	162.4	399.2	0.0311	210.6	3.09	143.8	1561.9	5610.4
Confidence	4.5	127.8	62.4	0.1703	103.1	73.5	112.5	276.6	0.0215	145.9	2.14	99.6	1082.3	3887.7
UCL	4.5	1424.8	1140.1	2.3455	-1604.1	866.8	3318.1	4378.5	-0.0180	3532.2	54.84	1661.8	4562.4	24967.1
LCL	4.5	1169.2	1015.3	2.0050	-1810.3	719.8	3093.0	3825.2	-0.0610	3240.4	50.55	1462.6	2397.7	17191.6
Mean	4.5	1297.0	1077.7	2.1752	-1707.2	793.3	3205.6	4101.9	-0.0395	3386.3	52.70	1562.2	3480.1	21079.4
Count	5.5	15	15	15	15	15	15	15	15	15	15	15	15	15
Std Dev	5.5	121.1	432.7	0.6523	176.5	83.1	153.3	203.4	0.0546	178.4	2.64	191.5	6670.7	9101.1
Confidence	5.5	61.3	219.0	0.3301	89.3	42.0	77.6	102.9	0.0276	90.3	1.34	96.9	3375.8	4605.7
UCL	5.5	596.0	1082.6	3.4563	-701.2	308.6	3670.7	2938.2	-0.0384	3875.8	60.05	1083.2	25854.3	56417.7
LCL	5.5	473.4	644.7	2.7961	-879.8	224.5	3515.6	2732.4	-0.0936	3695.2	57.38	889.4	19102.7	47206.3
Mean	5.5	534.7	863.7	3.1262	-790.5	266.5	3593.2	2835.3	-0.0660	3785.5	58.72	986.3	22478.5	51812.0

UCL 95 % upper confidence limit, LCL 95% lower confidence limit, Av Mean (average) value

Table 40 Used Ansell PVC gloves - Effect of position on five indices

Statistic	Position	Midpoint Time	Midpoint Value	Slope	Intercept	Break-through Time	Max Point	Max time	Top Slope	Top Intercept	SSperm	Lag Time	Integral_20min	Integral_30min
Count	1.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
UCL	1.0	1898.5	1104.2	1.5	-1240.1	1137.0	2948.0	7541.3	0.0	3074.1	42.6	2068.2	3127.1	13457.8
LCL	1.0	1612.2	799.5	1.2	-1446.8	932.6	2786.6	6185.6	0.0	2842.8	38.2	1869.2	2026.2	9619.1
Av	1.0	1755.3	951.9	1.3	-1343.5	1034.8	2867.3	6863.5	0.0	2958.4	40.4	1968.7	2576.7	11538.4
Count	1.5	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
UCL	1.5	2377.1	989.0	1.2	-1250.1	1544.9	2702.8	8102.1	0.0	2767.1	36.2	2490.4	1421.1	5301.2
LCL	1.5	2001.7	670.7	0.9	-1667.5	1264.9	2079.8	6255.2	0.0	2106.7	26.4	2249.7	501.9	2846.0
Av	1.5	2189.4	829.8	1.1	-1458.8	1404.9	2391.3	7178.6	0.0	2436.9	31.3	2370.0	961.5	4073.6
Count	2.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
UCL	2.0	809.8	743.2	2.3	-433.7	494.5	3605.1	3670.8	0.0	3676.6	45.1	1910.9	9695.9	25034.0
LCL	2.0	465.0	203.9	1.3	-1122.3	316.0	3246.7	3277.2	0.0	3376.2	40.4	1754.4	5744.5	18608.1
Av	2.0	637.4	473.6	1.8	-778.0	405.2	3425.9	3474.0	0.0	3526.4	42.8	1832.7	7720.2	21821.0
Count	3.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
UCL	3.0	1464.6	1169.2	2.2	-1413.5	895.9	3268.8	4446.7	0.0	3483.7	47.9	1684.8	7659.9	29445.3
LCL	3.0	1050.2	732.9	1.9	-1785.6	677.7	3144.0	3904.7	-0.1	3195.3	45.9	1379.0	3460.6	18581.3
Av	3.0	1257.4	951.1	2.0	-1599.5	786.8	3206.4	4175.7	0.0	3339.5	46.9	1531.9	5560.3	24013.3
Count	3.5	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
UCL	3.5	1567.7	1311.4	2.1	-1403.8	926.9	3173.1	4979.4	0.0	3346.1	48.0	1767.0	6173.0	22807.1
LCL	3.5	1307.2	972.7	1.7	-1732.2	733.2	2965.1	4109.7	0.0	2904.5	44.4	1505.5	2656.2	15521.9
Av	3.5	1437.4	1142.1	1.9	-1568.0	830.0	3069.1	4544.6	0.0	3125.3	46.2	1636.3	4414.6	19164.5
Count	4.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0
UCL	4.0	1108.4	1114.1	2.5	-1166.7	636.3	3486.1	4401.4	0.0	3811.8	45.9	1371.6	11380.1	33750.7
LCL	4.0	883.3	849.8	2.1	-1455.3	509.9	3331.3	3630.0	-0.1	3454.0	37.9	1145.7	6952.0	24096.9
Av	4.0	995.9	982.0	2.3	-1311.0	573.1	3408.7	4015.7	0.0	3632.9	41.9	1258.6	9166.0	28923.8
Count	4.5	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
UCL	4.5	1276.6	1128.3	2.3	-1002.4	740.5	3378.6	4198.9	0.0	3625.7	49.1	1479.0	13463.8	36413.6
LCL	4.5	836.9	700.4	1.9	-1579.2	493.8	3223.2	3710.7	-0.1	3345.1	47.2	1139.4	6603.4	23457.7
Av	4.5	1056.8	914.3	2.1	-1290.8	617.1	3300.9	3954.8	-0.1	3485.4	48.1	1309.2	10033.6	29935.7

15.8. Appendix H: Main Trials Data

15.8.1. Correlation Analysis using SAS (GLIM model)

The section of spreadsheet below is the top left hand corner of the spreadsheet on the next page showing some of the correlations (*difference and probability* below it) for some of the Breakthrough Time combinations of . New or Used, Position and Glove Type. Probabilities of less than 0.01 or 99% probable are taken as significant.

It should be noted that the sheet over page has a transcription error from combining some 200 pages of computer output. It is there to show the amount of data only. The problem with correlating everything with everything - here the correlates were New or Used, Position and Glove Type. As we were not able (through time constraints) able to make measurements of every permutation, let alone the desired eight measurements, the size of the matrix is a lot smaller than could be achieved. For the glove we collected (5 types), there would be $2 \times 5 \times 10 \times 8 = 800$ trials and needed to fill in the matrix with 100 columns. A veritable forest of data! What we have done, within the time constraints of the project, is to extract correlations from the data where we had adequate numbers of measurements to look at trends. This is shown in Table 9 “Number of Measurements”.

The code for the table is shown below:

Table 41 Codes for table columns

ode	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
os	1	1	3	3	5	1.5	1.5	2.5	3.5	4.5	5.5	5.5	1	1	2	2	3	3	4	4	5	1.5	2.5	3.5	3.5	4.5	4.5	5.5
ype	1	2.5	1	2.5	1	1	2.5	2.5	2.5	2.5	1	2.5	1.5	2.5	1.5	2.5	1.5	2.5	1.5	2.5	1.5	2.5	1.5	1.5	2.5	1.5	2.5	1.5
ew	1	1	1	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

Table 42 Section of Correlation Table

INDEX	POS	1	2	3	4	5	6	7	8	9	10
BT	1	.	3.5430	1.3543	3.2396	(3.2182)	7.3807	(0.0200)	3.0794	1.1897	4.5651
BT	P		0.0005	0.1768	0.0014	0.0015	0.0001	0.9840	0.0023	0.2352	0.0001
BT	2	(3.5431)	.	(1.9904)	(0.0211)	(5.4396)	5.1335	(3.0962)	0.6064	(1.0610)	2.0026
BT	P	0.0005		0.0476	0.9832	0.0001	0.0001	0.0022	0.5448	0.2897	0.0463
BT	3	(1.3543)	1.9904	.	1.8120	(4.0748)	6.1693	(1.2314)	1.9736	0.2321	3.3538
BT	P	0.1768	0.0476		0.0711	0.0001	0.0001	0.2193	0.0495	0.8167	0.0009
BT	4	(3.2396)	0.0211	(1.8120)	.	(5.2685)	4.8290	(2.8868)	0.5900	(1.0090)	1.8935
BT	P	0.0014	0.9832	0.0711		0.0001	0.0001	0.0042	0.5557	0.3139	0.0594
BT	5	3.2182	5.4396	4.0748	5.2685	.	8.0445	3.0550	5.1153	3.6193	6.1463
BT	P	0.0015	0.0001	0.0001	0.0001		0.0001	0.0025	0.0001	0.0004	0.0001
BT	6	(7.3807)	(5.1335)	(6.1694)	(4.8290)	(8.0445)	.	(6.7559)	(3.3869)	(4.3796)	(2.5703)
BT	P	0.0001	0.0001	0.0001	0.0001	0.0001		0.0001	0.0008	0.0001	0.0107
BT	7	0.0200	3.0962	1.2314	2.8868	(3.0550)	6.7559	.	2.8679	1.1366	4.1857
BT	P	0.9840	0.0022	0.2193	0.0042	0.0025	0.0001		0.0045	0.2567	0.0001
BT	8	(3.0794)	(0.6064)	(1.9736)	(0.5900)	(5.1153)	3.3869	(2.8679)	.	(1.3211)	1.0073
BT	P	0.0023	0.5448	0.0495	0.5557	0.0001	0.0008	0.0045		0.1876	0.3147
BT	9	(1.1897)	1.0610	(0.2321)	1.0090	(3.6193)	4.3795	(1.1366)	1.3211	.	2.2809
BT	P	0.2352	0.2897	0.8167	0.3139	0.0004	0.0001	0.2567	0.1876		0.0234
BT	10	(4.5651)	(2.0026)	(3.3538)	(1.8935)	(6.1463)	2.5703	(4.1857)	(1.0073)	(2.2809)	.
BT	P	0.0001	0.0463	0.0009	0.0594	0.0001	0.0107	0.0001	0.3147	0.0234	
BT	11	0.9638	2.7100	1.6877	2.6447	(1.4693)	5.1924	0.9196	2.7873	1.6432	3.5668
BT	P	0.3360	0.0072	0.0927	0.0087	0.1430	0.0001	0.3587	0.0057	0.1016	0.0004
BT	12	(7.8770)	(5.2338)	(6.3244)	(4.6715)	(7.9538)	1.3735	(6.8562)	(2.7603)	(3.9100)	(1.7575)
BT	P	0.0001	0.0001	0.0001	0.0001	0.0001	0.1708	0.0001	0.0062	0.0001	0.0800

15.9. Appendix I: Glove Papers by Investigators

Not included in this version

(These papers have been included as they are referred to in the report and are only published as conference proceedings. They were the genesis of this project.)

15.10. Appendix J: FTIR Output

Not included in this version

The attached sheets show the FTIR data from

- the fractionated solvents (Croda paint thinners and Gunwash) from the solvent recovery plant visited with the Pilot Trials
- the trials with mixtures.

The data was not used in the project due to file format difficulties and time constraints

15.11. Appendix K: Statistical Tools

15.11.1. Sample Size

The Following approach is taken from Kirkwood (Kirkwood 1988)

The required sample size for each group when comparing two means is

$$n = \frac{(u + v)^2 (\sigma_1^2 + \sigma_2^2)}{(\mu_1 - \mu_2)^2}$$

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
- v = percentage point of the normal distribution corresponding to the (two sided) significance level
e.g. if significance level = 5% ($\alpha = 0.05$) then v = 1.96 from tables
- σ_i = standard deviation of population *i*
- μ_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.

15.12. Appendix L: Software Disk - GloveTest program and Data

Program not included in this version

A demonstration program disk has been included in a pocket on the back cover of this report. It puts you in the driving seat of the *GloveTest* rig and allows you to see a speeded up version of the eight channel data acquisition (you didn't really want to sit there for four hours, did you?) and see the permeation curves from an real test run develop in a graphical form on the screen.

The program is fully functional, except that some elements such as the data analysis module have been disabled. You can modify flush times, sample times, switch off cells or print the display at any time during the run. The program reads data from eight files - data1 to data 8, corresponding to the eight channels of the *GloveTest* rig., rather than from the rig itself. The files data1 to data8 contain the output of the A-D converter which gives photoionisation detector, flow and temperature information and comments for each run. Reading the files is done at an accelerated rate for your convenience.

The setup file installs the program in a directory called DEMO on your hard disk drive C: and the program appears as an icon. To run the *GloveTest* program, click on the icon. You will be prompted to inject solvent in each cell and you start each cell with a mouse click or pressing the ENTER key. This starts a separate timer for each cell. The button marked PANIC is operational if you wish to terminate the program.

Things to watch for:

- The graphical display for each cell will appear to only show the flow (red line) through each cell at first. No solvent has yet been detected. The solvent breaks through at about "10" minutes (blue curve), the, the integral of the permeation curve also starts to become visible at about "20 minutes". Steady state conditions have developed by "50" minutes.
- The graphs automatically scale as the experiment progresses and the differences between sample are evident.
- The HNU photoionisation detector and flow meter both show as thermometers with an additional numeric display. The flow temperature under them is just digital.
- Flushing of the collecting manifold occurs at programmed intervals to prevent cross contamination. The flush status shows in a box.

Computer requirements

386 or better, with at least 2M of memory and 2Mb hard disk space and a colour monitor and Windows 3.1

- The screen dumps over page show what sort of screen you should be seeing.
- This disk also contains data from the project in the sub-directory DATA.