

THE UNIVERSITY OF MANITOBA

STUDIES ON TEXTILE STABILIZATION OF ENVIRONMENTAL
MALODORS FOR SENSORY AND ELECTRONIC NOSE ANALYSES

by

ROBERTA KATHLEEN YORK

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**“Studies on Textile Stabilization of Environmental Malodors for Sensory and Electronic
Nose Analyses”**

BY

Roberta Kathleen York

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfillment of the requirement of the degree**

Of

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Dedication

I would like to dedicate this dissertation to my late parents, Jack and Magdalena York, for all of their support and to Professor Marion Vaisey Genser, Professor Emeritus, University of Manitoba.

Abstract

The purpose of the research was to understand the role that cloth swatch testing and electronic nose analyses could play in environmental testing for agricultural malodors. Environmental malodors are a problem whenever large-scale production and residential areas lie near each other. Current sampling methods for these malodors can be cumbersome and expensive. This thesis describes a series of five studies related to stabilization of environmental malodors on cloth swatches and sensory and electronic nose measurement with an Alpha MOS Fox 3000 system, of the presence and intensity of the odors adsorbed onto fabrics.

In the first study, a 1-butanol reference scale, commonly used in environmental testing for magnitude matching, was evaluated using two sensory ratio scaling methods, magnitude estimation and the labelled magnitude scale. Calculated values of the exponent (n) of Stevens' Law, 0.59 for magnitude estimation and 0.46 for the labelled magnitude scale, were found to be statistically different at $p < 0.001$, although well within the range of values reported in the literature.

In the second study, 13 fabrics (cotton flannel, cotton broadcloth, cotton T-shirt knit, cotton terry cloth, cotton twill, worsted wool flannel, wool challis, silk habutae, linen suiting, spun viscose challis (rayon), Dacron type 54, spun polypropylene, activated carbon cloth) were evaluated for their ability to adsorb malodors when exposed to swine odor simulant under controlled conditions. Two sensory scales (difference-from control for linear data and labelled magnitude scale for ratio data) and electronic nose analysis were used to compare fabrics both within and between sample sets. All fabrics adsorbed odor to some degree and both sensory panels and the electronic nose were able to detect the changes. Groupings of fabrics for most and least effectiveness could be identified; however, fabrics that received sensory scores in the mid-range were not distinguishable. When physical attributes of all tested fabrics were related to the sensory scores, those with lower fabric weight and density and higher air permeability were identified as being most useful, and when tested within cottons, important factors were lower

fabric weight and higher air permeability. Substantivity of odors was shown for the short term in the second study by evaluation of the successful re-use of sensory samples up to four times.

In the third study, the available GC/MS was unsuccessful in providing the headspace composition of the sensory and electronic nose samples of the swine odor simulant-exposed fabrics. Data manipulation the electronic nose sensor signals allowed removal of the cloth signal from the exposed cloth signal. When compared to the signals for the swine odor simulant components, the spun polypropylene mapped most closely with the largest group of components.

In the fourth study, field testing involved selected cloth swatches being exposed to malodors simultaneously with the collection of sensory data during an odor dispersion study. When electronic nose analysis was compared to sensory results for actual field conditions, activated carbon cloth was found to be the most appropriate of the cloth sources tested.

In the final study, the effect of surface chemistry on the adsorption of odors was evaluated through changing a hydrophilic fabric (cotton flannel) and a hydrophobic fabric (spun polypropylene) through He/O₂ and He/ C₃F₆ exposure in a radio frequency glow discharge plasma polymerization unit. Surface changes in fabrics were validated through contact angle measurements and ESCA analysis. Cotton flannel showed no change in odor uptake as a result of treatment; however, both treatments increased odor uptake for spun polypropylene. It was also found that long-term substantivity for samples, stored in the laboratory and evaluated using the electronic nose, did not extend beyond one day for most of the samples without changes beginning to occur in the test results. The exception was spun polypropylene treated with plasma polymerization, where both treatments appeared to be stable up to four days. Both spun polypropylene and activated carbon cloth showed the most promise as suitable cloth substrates for laboratory and field sampling respectively.

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Chapter 1

Introduction

1.1 Perception and Measurement of Odor

Odor perception in humans is one of the most ancient senses and one that historically was useful in identification and protection. The process includes the signal being first received in the limbic system of the brain, that is, the area in which emotional responses occur and which is associated both with memory and with physiological responses that are independent of conscious decisions. From there it passes to the neocortex for labelling, etc. The basic pathway is well understood, but current research is clarifying the nature interaction at the receptor site and the mechanism of perception. The malodors of swine production facilities are those of waste products and as such have a strong emotional response associated with them. The root of the problem of the hedonic response to malodors from large-scale hog rearing operations lies deeper than a simple like/dislike response on a sensory ballot. It is connected with the basic emotion of “disgust” that has been studied and discussed in depth, especially by Paul Rozin and his co-workers (Rozin et al., 1994, Haidt et al., 1994, Rozin, 1996, Rozin et al., 1997, Rozin et al., 1999). The association of odors with body wastes – human or animal – falls into the realm of disgust.

1.2 Background on Environmental Malodors from Agricultural Sources

The intensive production of livestock, such as hogs, creates environmental problems for residents in the vicinity of these operations through the odors created by the large amounts of livestock waste products and the difficulties of effectively neutralizing these products. The livestock industry in Manitoba has seen a large growth in hog production over the last 15 years, with the numbers of animals expected to rise to 8 million hogs by the year 2005. The figures for 2003 show that the number of hogs is already at 7.3 million (Manitoba Department of Agriculture, 2004). This growth is due to several factors including the growing world demand for

high quality Canadian meat products and the effect the end of the Western Grain Transportation Act has had in enhancing the production economics for greater western livestock production (Manitoba Department of Agriculture, 1997). This increase in hog production brings with it inherent odor problems and the need to ameliorate them for the sake of local residents and to ensure the viability of operations at locations convenient to transportation and further processing.

The effects of these odors are more than aesthetic in nature (Sweeten & Miner, 1993). Malodors from intensive hog production operations have been shown in the literature (Schiffman et al., 1995) to negatively affect the moods of local residents resulting in more tension, depression, anger, fatigue, and confusion and less vigor than control subjects. The concerns of residents extend also to anticipated problems in resale values of real estate. Examples are given in two newspaper articles. The first was from October 24, 1997 Saskatoon StarPhoenix in a story regarding a proposed 1200-animal hog-rearing facility in R.M. of Hanover (southern Manitoba), which quotes a resident on adjacent property as concerned regarding the major problems from the facility and the resulting decrease in property values. A further fear quoted was that the Hanover council would ignore residents' concerns and quietly approve the barn. The odors (and potential odors) from hog rearing facilities are also the subject of legal proceedings. A second was from an October 25, 1997 article in the same newspaper, describing a court injunction being sought in Saskatchewan to halt a 12-million dollar project near Kelvington, Saskatchewan, which consists of two facilities, each capable of raising 8000 hogs. The injunction was being sought by one provincial department, Environment and Resource Management, as a result of community action, against a company that has the support of another provincial department, Agriculture. These examples are given to show the far-reaching effects of these operations and the level of investment in just one facility. The problems associated with these operations are many, with odor being a very significant component and often the first identified as a concern. Since this time, there has been publicity of varying sorts including television documentaries such as the CBC Television "The Nature of Things – Factory Farming" in January 2004, "The Fifth Estate –

The Sty's The Limit” on October 13, 1998 and CBC Radio “This Morning – Factory Farming” on February 9, 2001. The control of odor problems that are inherent with the increase in hog production is essential to ensure the viability of operations at locations convenient to transportation and further processing.

Odor has also been discussed as a source of health complaints. Schiffman et al. (2000) summarized the results of a workshop on the current knowledge regarding the health effects of odors. They outlined three situations or paradigms; symptoms which were related to odorants at levels that caused irritation or other toxicological effects, symptoms which were related to odorant levels which did not cause irritation, and symptoms which were caused by the presence of a co-pollutant. Each of these situations could be operating in the case of agricultural malodors and the odor served as the “exposure marker” for each of them.

Environmental regulators were also concerned with the appropriate levels of odorant in terms of setting standards for agricultural production facilities. These levels must take into account the local implications of production on residents who are impacted by odors carried by the wind and how this odor spreads and dissipates. The level at source and at specific distances to which the regulations are set depends on the human response to these odors – and odor measurement is part of this process.

1.3 The Effects of Odor and Malodor on Humans

The effects of odors and the memories and emotions produced by odors have been studied from different view-points and all feed into the same conclusion – that odor and emotion are connected and that humans respond to emotions in a manner which is physiological and can be traumatic. The trauma arises from the implications of the malodors that can induce stress. Schiffman et al. (1995) examined the psychological effects of livestock malodors on near-by residents using a psychological profiling method (“Profile of Mood States” questionnaire) through which ratings on tension/anxiety, depression/dejection, anger/hostility, vigor/activity,

fatigue/inertia, and confusion/bewilderment were measured. All of the indicators increased on exposure to malodors except for vigor, which decreased. The possible factors cited in mood changes were (a) unpleasantness of odors, (b) intermittent nature of stimulus, (c) learned aversions to odor, (d) potential neural stimulation of immune responses, (e) direct physical effects - nasal and respiratory irritation, (f) possible chemosensory disorders, and (g) unpleasant thoughts associated with odor (e.g. loss of property value).

In considering malodors, some aspects of current research shed light on human responses to pleasant and unpleasant odors and on the effects of concentration on odor annoyance. Different parts of the brain respond to pleasant and unpleasant odors (Schiffman, 2004, Royet et al., 2001). Sobel et al. (2003) extensively reviewed and summarized new neuroimaging techniques as applied to odor perception. Techniques such as positron emission tomography and functional magnetic resonance imaging have been used to study the areas of the brain activated by odors. Studies show that all odorants activate areas of the anterior olfactory nucleus and the olfactory tubercle, while only unpleasant odors activated the amygdala and neighboring areas. They also showed work in which odorant-induced activation was greater in women than in men and that the degree of activation in the cerebellum was concentration-dependent for propionic acid.

Bensafi et al. (2002) compared electrophysiological and psychological responses to pleasant (cineole, menthol, or isoamylacetate) and unpleasant (thiophenol, isovaleric acid, or pyridine) odors. The test subjects either sniffed the odor with no judgement required, sniffed the odor and assessed pleasantness (affective judgement), or sniffed the odor and assessed familiarity (cognitive judgement). Unpleasant odors resulted in an increase in heart rate when pleasantness was assessed but not when familiarity was assessed. Their results indicated that differing pathways were involved when affective judgements but not when cognitive judgements and that emotional response to odors resulted in an involuntary categorization based on pleasantness.

Studies of behavioral responses to odor show some of the responses in the form of pleasant/unpleasant categories – and these show consistencies across cultures. Schleidt et al. (1988) used interviews with Germans (166 subjects) and Japanese (88 subjects) and asked for pleasant and unpleasant odors from memory and their associations about them. They used open-ended questions and participants were asked to name as many odors as they wished and in any sequence. They were further asked, “why the odor was pleasant or unpleasant”, “was it connected to a special situation”, and “what else they wished to say about the odor”. They collected 2040 different odor responses and categorized them. Categories that occurred in both cultures and the odors associated with them accounted for 2/3 of the responses and are identified in Table 1.1. The most unpleasant odors were “decomposed” and “fecal”. Odors that were different culturally were mainly those associated with fragrances and soaps (intensity, especially) and some specific food items. Given this agreement on the nature of pleasant and unpleasant, it is possible to consider a measurement scale for this odor attribute.

Table 1.1 Cross-cultural responses to odor quality (Schleidt et al., 1988)	
“uniformly pleasant” odors	“uniformly unpleasant” odors
civilization (intimate situation at home – bed, bath, clothes),	civilization (smell of exhaust fumes and smoke)
food and drink (grilled and roasted protein food, fruit and spices, pastries and coffee/tea),	food and drink (odor of burnt and deteriorated food, especially protein and odor of onion and garlic)
nature (smells of streams, lakes, sea, air/earth, plants),	nature and “man” (odor of excrements of animals and man as well as body odor and sweat, mainly of strange people in a crowded situation e.g. in a subway)
“man” (odor of specific individuals, e.g. husband, friend, child).	Other (smell of rubbish and deteriorated things)

1.4 Project Objectives

This work explores various aspects of a test method that has the potential for wide range application in environmental testing of air-borne odorants not only from agricultural malodor sources, but also in the assessment of other sources of air-borne contamination. There is limited

information in the textiles research literature on the adsorption and desorption of odors relative to textile substrates. There is a need to understand how the structural characteristics of a textile, its surface area and topography, the nature of its fibre composition as well as its surface chemistry might influence such phenomena. This knowledge can of use in other textile applications, such as protective clothing, where the adsorption of odors is considered either desirable or, alternatively, undesirable. There is also a need in the sensory literature to clarify the roles that different forms of sensory analysis contribute to the characterization of the nature of environmental off-odors and their intensity measurement.

The purposes of the various components of this work all relate to the assessment of the usefulness of cloth swatch sampling as a field sampling system for the study of environmental malodors. This is accompanied by work with a new methodology that has been applied to malodor assessments to a limited degree, the sensor-based system known as the electronic nose.

Environmental malodors are important, both to the industries that produce them and the people who are resident in areas that are impacted by these odors. There are several ways in which the presence and/or intensity of these odors have been measured including sensory panel measurements in the field, various types of laboratory measurements using humans including olfactometer measurements of air samples taken in the field, and gas chromatography of the components of air samples from malodor sites.

The purpose of this project is to look at the development of a new method for sampling airborne malodors. The work combines methodologies from several domains including sensory science for the objective methodologies for sensory analysis of taints and malodors, textile science for physical and chemical characteristics of fibres and fabrics affecting odor uptake, and bio-systems engineering for systems to reduce and eliminate sources of air and water pollution that provide the sources of test situations and the technology of air sampling.

In considering the approach to this work, a series of questions were developed to be investigated in a series of studies. These were identified as the work progressed and relate to the assessment systems used to measure odor uptake.

1. How do different scaling systems perform for sensory measurement of malodors? Humans perceive most sensory stimuli on a log scale and most studies relating sensory perception of intensity to physical measurements rely on this fact. A new measurement method has been developed by Green and co-workers (1993, 1996) based on the work of Georg that allows the collection of sensory intensity data that is ratio scaled but using a pen and paper system. It has performed well in other systems, and we will evaluate it here compared to standard magnitude estimation methods.
2. How do different types of cloth perform for the uptake of odors? Is there a fibre that is better for this and are there any physical properties of the cloth, which will help, predict this performance?
3. Are there differences in the odorants that different fibres or cloth types will adsorb? Which components are most easily adsorbed and released into the system and how can this be assessed?
4. How well does this laboratory methodology carry forward into actual field-testing? Can cloth types identified under laboratory conditions be successfully utilized an actual odor dispersion test format?
5. Can cloth surfaces be made to adsorb odors more efficiently for this work?
6. Which measurement systems will allow odors to be evaluated? New technology in the form of sensor-based electronic nose technology is available. How well does this compare to the use of human assessors for the presence and intensity of malodors sampled from the environment?

The specific objectives include the development of the components for a method of standardized odor sampling of air-borne malodors using a range of appropriate standardized

fabrics as cloth swatches and testing it through analytical sensory analysis and the application of electronic nose technology. The method includes stabilizing swine odor on cloth swatches by exposure to controlled amounts of odorous air so that the odor can be removed from the sampling area and taken to a sensory facility for evaluation.

1.5 Overall Experimental Design

The study will provide information from which protocols for sensory evaluation of airborne malodors can be established. It will also provide another application by which to evaluate the role of the emerging electronic nose technology for monitoring malodors. The use of the electronic nose in this work will allow the systems to be evaluated in a different way and to be compared to the results from the sensory panel.

The work is divided into the following sections:

Study #1: Evaluation of Two Ratio Scaling Methods Using a Standard 1-Butanol Scale and the Electronic Nose (in Chapter 3). This study compared the use of two ratio scaling methods for a scale based on 1-butanol concentrations, a compound that is commonly used as a reference chemical in environmental testing. The hypothesis was that the data from the labelled magnitude scale would provide the same result for the calculation of the exponent of Stevens' power law as the data from magnitude estimation. The sensory results were compared to electronic nose analyses of the samples to evaluate the way in which each of the scaling methods relates to the sensor responses. This was done through linear regression subroutines in the data analysis software.

Study #2: Evaluation of Cloth Sources for Uptake of Malodors in Environmental Testing (in Chapter 4). The focus of this study was the comparison of a selected set of 13 fabrics of varying fibres and structures for their ability to adsorb and retain odor from a swine odor simulant through sensory and electronic nose analysis. The set of fabrics was tested along with the commonly used

fabric (cotton flannel) for the ability of the fabric to adsorb swine odor and compared for the relative strength of the odor adsorbed among the 13 fabrics. Odor intensity was measured using both the labelled magnitude scale and the difference-from-control test to compare the sensory results from a ratio and a linear scaling method. As part of the study, the exposure system to treat the fabrics was modified from previous work and the swine odor simulant was developed for fabric exposures. Testing methodologies were developed for the use of the electronic nose. Sensor responses were compared to sensory panel results from the two scaling systems used. Standard textile evaluation methods were used to characterize each of the samples and to provide physical data to relate to the sensory and electronic nose measurements of odor retention on the fabrics.

Study #3: Evaluation of the Headspace Composition of Odors from Cloth Swatch Samples (in Chapter 5). When the cloth swatches to the swine odor simulant, they were exposed to a mixture of chemicals which represent certain major components of this malodor. The purpose of this study was to attempt to specify which of the odorant components of the swine odor simulant are being retained by the cloth swatches and released into the headspace to form the sample that the panelists and the electronic nose actually received. Both GC/MS and electronic nose analysis were tested for this purpose.

Study #4: Field Testing and Electronic Nose Analysis of Selected Cloth Swatches (in Chapter 6). In this study, selected cloth swatches were evaluated under actual field-testing conditions for their ability to adsorb and retain an environmental malodor. Selected cloth swatches were attached to specially constructed field vests worn by a fifteen-member odor dispersion panel so that sensory data and cloth swatch could be performed simultaneously. The cloth swatches were then analysed with the electronic nose and the sensor responses compared to the sensory data from the

field panel. Comparisons were made to the position of each of the assessors in the field and the degree to which each cloth swatch adsorbed and retained the environmental odor.

Study #5: Modification of the Surface Chemistry of Selected Cloth Swatches using Plasma Polymerization (in Chapter 7). In this study, the actual surface chemistry of two fabric types, cotton flannel and spun polypropylene, was modified using plasma polymerization methodology. The resulting treated swatches were compared for odor adsorption using the swine odor simulant described in Chapter 4 and tested for odor uptake using the electronic nose. A second study in this section was done to evaluate the stability of selected test samples for odor evaluations for a series of holding times before analysis.

1.6 Definitions

Some terms have been used throughout the thesis in a way that has a particular meaning in textile science. The following attempts to define them as they are used in the chapters, which follow.

1. *Stabilization* - in the context of this work, this refers to the adsorption of an odorant on to a textile surface in order to transport the odor from the location of sampling (laboratory or field location) to the location of analysis (laboratory – either sensory analysis or electronic nose).
2. *Substantivity* – is not specifically defined in the literature, but is rather described in slightly different ways for the evaluation of perfumes on skin and scented products for laundry use. Ormancey et al. (2000) describes it as the amount of time a perfume remains perceptible on a support or as the ability of the odorant to remain adsorbed on the support for extended periods of time. As used in this manuscript, this term includes the sample remaining unchanged in its odor pattern of character and intensity from the original condition of the sample.

3. *Adsorption* and *release* of odors from the cloth surface – the means by which an odorant is held on the surface of the cloth and then the rate at which the odorant is volatilized from the surface of the cloth used for sampling the odors.
4. The substantivity process between an odorant and its support is *adsorption* > *retention* > *release*. The time frame for this process is not known for the cloth samples and odorants used in this work. The assumption is made that the samples are stable for the duration of the day of preparation and testing.

The relationship between stabilization and substantivity can be thought of as *stabilization* is the act of the odor adsorbing onto the cloth and *substantivity* describes its behavior while it is adsorbed, including both length of time it is perceptible at its original intensity and the constancy of the odor character.

There are some abbreviations that are used throughout the manuscript for the identity of the cloth swatches, the swine odor simulant components, and certain other standard chemicals used in the work. While attempts are made to minimize the usage of these abbreviations, they are part of the work within the electronic nose data analysis software and appear in the principal component analysis maps and regression graphs from these analyses. Table 1.2 contains lists of these abbreviations for the cloth samples, the swine odor simulant components and the electronic nose analysis methods for reference throughout the following chapters. The results from the electronic nose analyses are easier to demonstrate when the comments are directly with the maps or graphs which are the source of the comments. This convention used for all the electronic nose results.

Table 1.2 Abbreviations used to identify specific fabrics and chemical compounds used in electronic nose analysis in the studies that follow.

Abbreviation	Identity of Sample
Cloth Swatch Fabrics	
ACC	activated carbon cloth
COT	cotton - flannel, bleached
CTB	cotton broadcloth, bleached, mercerized, combed
CTK	cotton - knit - bleached cotton T-shirt fabric
CTT	cotton - 9.5 oz, bleached terry cloth
CTW	cotton - twill, bleached, mercerized
DAC	Dacron type 54 (disperse dyeable)
LIN	linen - suiting
PLY	spun polypropylene
RAY	spun viscose challis (rayon)
SLK	silk habutae 8 mm
WLC	wool challis
WOL	wool - worsted flannel
Swine Odor Simulant Components	
ACE	acetic acid
BUT	butanoic acid (n-butyric acid)
CRE	4-methyl phenol (p-cresol)
IND	indole
ISB	2-methyl propanoic acid (isobutyric acid)
ISV	3-methyl butanoic acid (isovaleric acid)
NH4	ammonium hydroxide (NH4OH) 5%stock solution
PHE	phenol
PRO	propanoic acid (propionic acid)
SKA	3-methyl indole (skatole)
VAL	pentanoic acid (N-valeric acid)
SOS	Swine odor simulant
Electronic Nose Data Analysis – as defined for the Alpha MOS Fox 3000 using AlphaSoft	
CQ	Concentration Quantification – the logarithmic regression model subroutine to relate sensor responses to other known values for the samples
DI	Discrimination Index – given as a percentage varying from –100% to +100%. This is given as an indicator of the differentiation among the samples in the principal component analysis subroutine.. Only discrimination index values above 80% are considered to be “good” results in terms of the differentiation among samples.
EN	Electronic nose, here the Alpha MOS Fox 3000 Electronic Nose
PCA	Principal components analysis subroutine
SSC	Sensory Score Correlation – the linear regression model subroutine to relate sensor responses to other known values for the samples
Plasma polymerization treated fabrics – Study #5	
COT	Untreated cotton flannel

C_F	Cotton flannel treated with helium/hexafluoropropane mixture (He/C ₃ F ₆)
CO2	Cotton flannel treated with a helium/oxygen (He/O ₂) gas mixture
PLY	Untreated spun polypropylene
P_F	Spun polypropylene treated with helium/hexafluoropropane mixture (He/C ₃ F ₆)
PO2	Spun polypropylene treated with a helium/oxygen (He/O ₂) gas mixture

Chapter 2

Review of Literature

2.1 Sensory Measurement of Odor Character and Intensity

The presence of malodors in the environment and the human response to them can be considered largely as a “hedonic” response i.e., a “like/dislike” response – with “dislike” being the operating condition in the case of malodors. At high concentrations this response can also be annoyance and discomfort. The measurement of these odors is an analytical response and can be considered under the same systems as other stimuli for quantification using sensory analysis.

Scaling systems provide a means of assigning values to stimulus intensity.

Stevens (1961) described four types of measurement scales for sensory stimuli:

1. identity – with names or labels to identify items or classes
2. order – reflecting the rank order of items
3. intervals – reflecting differences or distances among items
4. ratios – reflecting ratios among items.

Scaling is a type of measurement used in psychological and psychophysical testing by which numbers can be associated with perceptions. Different ways have been identified in which humans can be used to generate measurements using scaling, rating, magnitude estimation, comparison, and production methods. These are accompanied by methods to evaluate the data through appropriate (statistical) analysis techniques.

Many workers have discussed the type of data collected. Torgerson (1958, p. 48) divided measurement into two groupings - stimuli and people, with a third grouping of ‘both together’ and gives the terms “judgements” and “responses” to the first two, respectively. In the stimulus-centered or judgement approach, the assessor is asked to evaluate the stimuli on some defined or designated attribute. The assessor responds to the sample or stimulus in terms of its relation to other stimuli on a defined continuum of intensity. Because the response to the stimulus is based on its relative position among other stimuli, the personal bias of the assessor is reduced. In the

response approach, the assessor or subject is asked “to respond to the stimulus on the basis of the position of the stimulus in relation to the subject’s own position with respect to the attribute.” In this case the assessor’s personal bias - attitudes, feelings, etc. - are part of the measurement. A situation of a “both together” grouping, which cannot be separated based on task set, is described by Torgerson as including preferences, aesthetic judgments, and judgements of pleasantness. In this case, he states that either of these two approaches might be used on a given set of data. It is the decision of the experimenter whether or not to consider these as judgements reflecting the position of the stimulus relative to others on a continuum, or whether to consider them as responses reflecting opinions that may differ with each subject.

These three groupings can be illustrated by the example of the measurement of carbonation in a popular beverage. In testing the stimulus, the level and type of carbonation can be measured (amount, size of bubbles, etc.), or the preference for a particular type of carbonation. Both can be considered if the issue of brand name is introduced into the assessment of carbonation, whereby the assessor may be swayed in the assessments by the presence of a favored brand in the test samples. This distinction is important in environmental testing – as the subject measurement or hedonic response at different levels gives information for regulatory decisions regarding levels of allowable emissions, while stimulus measurement gives information regarding the actual condition of the emissions.

In sensory science, this distinction of test methods guides the question being asked, and leads to the type of test that should be used. The first two groupings correspond directly to the classification of “subjective” and “objective” sensory testing, or of hedonics vs. intensity.

Sensory tests are generally used for one or a combination of three basic aspects of odor: intensity, character and pleasantness.

1. Intensity – either the intensity of the overall odor or the intensity of specific character notes.
2. Character – the nature of the odor (i.e., the specific description of the overall odor or of a specific component).

3. Pleasantness – this can be either a hedonic or an analytical response. The use of the term “hedonic tone” is common in environmental testing. Recent work in neuroimaging and physiological responses to odor has brought some light into this area and shows that unpleasant odors actually cause physical responses in the perceiver (as discussed above).

In sensory measurements of environmental malodors, the general measurement is intensity of the stimulus and various methods are described for performing these measurements. Some measurements also include the pleasantness aspect that is called “hedonic tone”. As discussed above, hedonic testing generally refers to like/dislike responses that indicated purchase behaviors towards products and that would be considered to be subjective sensory analysis. In this case, “hedonic tone” actually refers to pleasantness/unpleasantness measures that are meant to indicate a specific attribute of the stimulus and that is then objective sensory analysis.

Pleasantness/unpleasantness can be described in terms of physiologic response and generally refers to perceptions of discomfort relative to the odor. As is seen in the work of Schiffman et al. (2000), increasing concentrations of components of swine odor result in a change in odor quality from threshold > annoying > physical irritation response. This change in odor quality corresponds more closely to a discomfort measurement than a hedonic one, so a change in terminology would indicate of the actual intention of the measurement. As was discussed above, human odor perception includes an “emotional” component as the odor signal passes through the limbic system in the perception process, and this is accompanied by a physiological response.

The difference between pleasantness and intensity testing is clearly illustrated in a paper by Doty (1975), in which the responses for perceived intensity and perceived pleasantness were collected using ratio scaling methods. Each of the 10 odorants tested showed a clear linear relationship (in a log-log analysis of the data) between physical and perceived intensity of each compound. It is also shown that the same type of plot for the perceived pleasantness data gave a curvilinear graph, which peaked at a unique point of maximum pleasantness for each compound. The differences between pleasantness and intensity responses are an important consideration in

the selection of which sensory testing approach is used for the study of malodors. These differences in approach are part of the two types of sensory testing, which are subjective and objective testing.

2.1.1 Subjective and Objective Sensory Testing

The first division of sensory testing is into subjective versus objective sensory tests. In this case, subjective tests are those which measure the opinion of a subject who is using a product and describes a response that is affected by personal bias, emotional background, etc. These are generally responses that describe the individual and are not necessarily validated through demonstration of ability. This term has often been used incorrectly to describe all sensory tests – presumably from the assumption that sensory tests measure with subjects and other tests measure using objects (laboratory equipment) and are called objective. Pangborn (1989) and Trant et al. (1981) have discussed this misinterpretation of terms.

This differentiation of subjective (often called hedonic testing) versus objective (presence and/or intensity testing) is essential in sensory analysis of products, because the nature of the test needed governs the questions which will be asked and manner in which the data can be analyzed and interpreted. If these two purposes are confused, the data will not be useful.

Hedonic testing in sensory evaluation is synonymous with subjective testing and defines those tests that evaluate the subject, not the sample or, in other words, the subject's feelings about the sample and its attributes. In this case, while detailed composition information may be available about the samples being used and assumptions may be made by the experimenter about what those levels of components might mean in terms of the product perception, there is no "right" or "wrong" answer about the sample. Whatever the assessor's subjective response happens to be is "correct".

Objective sensory testing is synonymous with intensity testing and measures the presence, or intensity, of specific characteristics. It implies a response that is based on external

phenomena or events and that, with training, is to be detached, impersonal, unprejudiced (the assessor does not have to “like” the product to evaluate it for particular defined levels of attributes). In sensory evaluation “objective” defines those tests that are based on results with selected, trained judges appropriate to the test procedure who are monitored for their performance throughout the test series.

2.1.1.1 Data Collection in Hedonic and Intensity Testing

Scaling methodologies have been an area of study in both psychology and sensory science (Dunn-Rankin, 1983; Lawless & Heymann, 1999; Meilgaard et al., 1999). Some basic definitions for use in this work are provided by the ISO Technical Committee 34/Subcommittee 12 in the document “ISO/WD 5492 – Sensory Analysis – Vocabulary” whereby:

Scaling – a method consisting of numbers or terms used to denote the strength of a perception.

Interval Scale – a scale where numbers or terms are chosen in such a way that equal numerical intervals are assumed to correspond to equal differences in sensory perception.

Magnitude estimation – a process of assigning values to the intensities of an attribute in such a way that the ratios between pairs of assigned values are the same as between the magnitudes of the perceptions to which they correspond.

Ratio Scale – a scale where numbers are chosen in such a way that equal numerical ratios are assumed to correspond to equal sensory perception ratios.

Ratio scaling - Method in which values are assigned to the intensity of attributes in proportion to the assessor's perception of the intensity of the attributes with or without reference to a selected standard (see Magnitude Estimation).

Both of hedonic and intensity data can be collected through testing that can be accomplished with a variety of scales, illustrating each of the types discussed including nominal,

ordinal, interval and ratio (Stevens, 1957). In the area of interval scaling, the data are collected using two different types of scales:

1. category scales – which can be structured or semi-structured, and
2. line scales – which can be unstructured or semi-structured.

The application of ratio scaling to sensory measurements of odor and taste began with the extensive work by Moskowitz and many publications since the late 1960's to current literature. Moskowitz was a student of Stevens and sought to take the information obtainable through ratio scaling and apply it to the practical problems sensory analysis needed to answer. This has resulted in studies that measure both the intensity perception and constants of Stevens' law and work that has carried this into the application of both hedonic (acceptability) testing and the description of sensory attributes. The methods used for data collection are the classic methods of ratio scaling.

2.1.2 Difference-from-Control Test

This test is described by Munoz et al. (1992), Meilgaard et al. (1999), Lawless & Heymann (1999) and Aust et al. (1985). This test relies on the availability of a clear known (i.e., untainted or untreated) reference sample against which all of the other samples can be tested. It is basically a difference test in which the degree of difference is measured as well as the presence of a difference. Often multiple samples are presented along with a control (or reference) at the same session. The degree of difference can be reported using verbal or numerical category scales or line scales. The difference from control test is a standard test used in a wide range of quality control applications for sensory testing of food and other products. It has been successfully applied in sensory evaluation of taints in fish that have been exposed to oil spills and to manufacturing (pulp and paper mill) effluent that has been released into rivers (Reilly & York, 2001; Environment Canada, 1997).

The advantage of this method over difference tests such as the triangle test for testing taints and malodors is that the nature of the difference required is easier to define (i.e., taint), and the assessor is less influenced by other factors in the sample. When trained panels and proper rinsing procedure are used, the difference from control test allows the presentation of multiple coded samples with the one reference sample. In tests such as the triangle test, the question is usually oriented to which sample is different rather than a specific defined difference and many more samples are required for the test. The data gathered can be analyzed through standard statistical tests to give measurements of intensity of taint relative to the control samples.

2.1.3 Magnitude Estimation

Magnitude estimation is the standard method by which ratio data are generated and has a long history in psychophysical research. It was developed by Stevens (1957) in studies relating the perceived and physical intensities of loudness and brightness and resulted in the derivation of Stevens' Law relating perceived and physical intensities of stimuli. This is given by the following formula:

$$S = k I^n$$

transformed to $\log S = \log k + n \log I$

where S = the perceived intensity of the stimulus,

I = the physical intensity of the stimulus,

n = the exponent governing the rate of growth of perception of the stimulus

k = a constant

Since Stevens development of this sensory relationship, it has been applied to a wide range of perceptual systems and the exponents published in several references including Moskowitz & Jacobs (1988), Meilgaard et al. (1999), and Lawless & Heymann (1999). Data from this method have been used to calculate the constants of Stevens' Law through linear

regression of the two variables using log-transformed data. The value of the exponent “n” is ideally unique for any given stimulus and can be compared between studies.

2.1.4 The Labelled Magnitude Scale

A new form of collection of ratio scaling data has been described by Green & co-workers (1993; 1996), in which the format of ratio scaling has been put into a labelled magnitude scale. This is essentially a linear scale in which the anchors are log-spaced for the terms used on the scale as shown below and in Appendices E and G. The terms used are presented on a line scale that is 25 cm long with the anchors positioned at these positions on the scale. The numbers are not present, only the words.

95.5%	strongest imaginable
50.1%	very strong
33.1%	strong
16.2%	moderate
5.8%	weak
1.4%	barely detectable

These scales have been compared to classical ratio scaling and have been shown to give the same exponent of Stevens’ power law for pain perception and for odor and taste. This works when the anchors are defined as the strongest imaginable as a general concept, rather than as being specific to the perception being tested within the sensory modality.

Some key features of this scaling method include the following:

1. It produces magnitude estimation data (ratio scaling data) that can be used to reflect the sensory system (we perceive in a ratio mode rather than a linear mode).
2. It is simpler to administer than classical magnitude estimation testing.
3. It allows single sample presentation.

4. It requires an appropriate specification for the endpoints of the scale – strongest ever of anything, not just strongest of that particular odor.
5. The resulting data can be handled in the same manner as those produced by magnitude estimation that means that normalization of the responses can be included in the data analysis.

2.1.5 Data Analysis for Ratio Data:

The use of normalization of magnitude estimation data (ratio scaling data) is an accepted practice in its analysis. It takes open-ended data and puts it onto a scale that is more “manageable” and it corresponds to the reformatting of Stevens’ power law into the slope-intercept form of a straight line.

The process of normalization can be done using the format of modulus equalization that is detailed by Moskowitz & Jacobs (1988). The objective is to normalize all the panelist’s ratings, so that the geometric mean of each panelist equals the geometric mean of every other panelist. All geometric means equal a predefined constant. The requirement is each panelist must evaluate the same stimuli. The steps in the process are as described by Moskowitz & Jacobs (1988).

2.1.6 Uses of 1-butanol scaling methods in odor research

Surveys of the literature on odor perception, reveal that 1-butanol may be one of the most studied compounds. Hummel et al. (1997) describe its use as part of the “Sniffin’ Sticks” test for olfactory performance. It is used by ASTM as a reference standard ASTM E544-99. It has been recommended in the past by Moskowitz et al. (1974) as a compound that could be used across odor studies to become the reference standard through which studies could be compared. This recommendation, however, has been utilized by other workers in subsequent years.

The 1-butanol scale used for cross-modality matching for odors is described in ASTM E544-99. Its purpose is to define a range of intensities of perception from “very weak” to “very strong” and to provide a standard method of referencing odor intensities in a matching standards

study. As stated in the standard, the intensity of the odorant is matched, while differences in odor quality are ignored. The scale can be used in its Static-Scale form, as water solutions presented for sniffing in glass flasks. (The other form is the Dynamic-Scale form, in which the samples are presented by an olfactometer.) The reference scale selected followed the recommendations in Section 6.3.6 of this standard in that the lowest concentration used is 10 ppm in water and the highest 20,000 ppm. The number of scale steps recommended here was 12 and this was the number of standards used

The static form of this scale, with 8 steps, is used as a standard reference scale in sensory testing of environmental malodors. The sensory panel is trained to the intensities of each of the steps in the scale and the field measurements of sensory intensity are made relative to the sensory intensity of this 8-point 1-butanol scale (St. Croix Sensory, Inc., 2000). The procedure of using a reference scale of one sensory stimulus and rating the intensity of another stimulus (such as another odor) to the intensity of a point on the first scale is known as magnitude matching.

Reasons cited in ASTM E544-99 Section X1 that 1-butanol was selected as the reference odorant for this standard include the following:

1. It is a common chemical and is readily (and inexpensively) available in 99+ mol % purity.
2. It is non-toxic, except in multi-gram doses.
3. It has good stability in the presence of air and water.
4. Its odor is somewhat “unrelated”, so that its odor quality can be more easily ignored when comparing with other odors that may have different qualities.
5. Most people do not object to sniffing it frequently during odor-intensity referencing.
6. Is perceived odor-intensity changes rapidly with concentration (i.e., the slope of the log-log plot of intensity vs concentration is greater than 1), so the scale covers a broad range of sensory intensities with a reasonable number of scale points. Also, a distinguishable intensity change occurs between samples using the factor of 2 difference.

7. Since its odor threshold is relatively high (2-6ppm vol/vol in flowing air at 100-200 mL /min), a continuous discharge of its vapors into the test room air does not result in a noticeable odor level in a normally ventilated room.
8. Its concentration in air, down to the odor threshold concentration level, can be monitored with hydrogen-flame ionization detectors without the need for preconcentration.
9. Another observation in an earlier version of the standard was that the odor is relatively “emotionally neutral”, evoking neither a high degree of liking or disliking.

All of these factors make this a useful tool in the measurement of intensities of environmental malodors.

2.2 Malodors and the Measurement of Environmental Impact

Sensory testing has a long history of application in the evaluation of the effect of environmental off-odors and off-flavors. Many papers have been published on results of analyses of environmental taints in aquatic systems. The origin of these taints can be either naturally occurring (e.g., resulting from algal blooms) or man-made (e.g., from manufacturing activities or as a result of environmental accidents/ oil spills) (York & Sereda, 1994). While in any research study, the selection of an appropriate test method is critical to the collection of useful data, there are many examples of data collection that have not been as useful as they could have been, even though the studies were carefully conducted, because the wrong questions were asked and confounding background effects were not taken into account (Environment Canada, 1997).

Sensory analysis of off-odors and off-flavors has some unique and difficult challenges, not the least of which is the complexity of the tainting or malodor source. It is seldom that a single or small group of compounds can be identified as the primary source of the malodor (or off-flavor), as in the case of the compounds 2-methylisoborneol and geosmin that cause muddy-earthly off-odors/flavors in water sources and fish tissue. It is more usual that the source is a complex mixture of compounds that are perceived by the human olfactory system at very low

concentrations. This is the case for the mixture of compounds that cause the malodors of livestock production.

A complex food product or chemical mixture is often analyzed through the use of highly trained assessors, either those selected and trained for descriptive analysis procedures or those trained to work as individual product experts. While both of these methods are effective, they are expensive to initiate and to maintain. In developing the testing methodology, it is desirable to establish a procedure that can be used with selected and trained panelists who are chosen for one sensory task and who do not require the level of training as the first two. Cliff & Heymann (1991), in a study on cat litter, utilized this third type of panel to measure a relatively complex system (the litter itself and the waste products). However, unlike the actual livestock odor under consideration, cat urine was essentially a strong ammonia odor that was relatively easy to define in testing. The complexity of the malodors in environmental testing has resulted in the use of matching scales, particularly the 1-butanol scale described above.

The problems of malodors from hog operations have become the subject of study in many locations and within many research groups over the last two decades. This is due to the development of large-scale hog rearing operations and the effects on the immediate and extended environment, both on the human population and on the land use in the affected area. The odors and effluent from the facilities are major problems for residents in the adjacent areas/neighborhoods. These problems fit into a variety of categories including monetary, physiological and psychological (Schiffman et al., 1995).

The control of odors from animal production that impact the surrounding areas is an ongoing aim of research in bio-systems engineering, animal nutrition and other associated disciplines. All of this work requires a means of measuring the effectiveness of the methods used – by measuring the odor intensity of the remaining odor conditions compared to the untreated state within the study and often to other similar studies. Assessments need to be meaningful not only within the context of a given study, but also in the context of studies done over time, over

different geographical locations and over ongoing developments in treatment methods to allow meaningful comparisons among data sets.

Currently there are two styles of measurement that are often used concurrently in studies. One is taking the assessors (or panelists) to the stimulus, i.e., the field location where the odor is present, and the other is to take the stimulus to the panel. The current standard method of this second type of testing environmental malodors utilizes large samples of air taken in sampling bags and transported to a laboratory for analysis with an Olfactometer. Such tests are generally well accepted and provide objective data when used with selected, trained assessors. The data produced is limited to the degree of dilution associated with perception – a measure of threshold for the odorant or mixture tested. This test produces an “odor number” which is a relative measure of the actual odor intensity. The disadvantage of the method is the size of the samples required and the expense associated with the disposable sampling bags. The addition of standards to this system allows calibration of the measurements and comparisons both within and across tests. As with any sensory test of the nature and intensity of a sample, it is essential that appropriate sensory tests be used, i.e., objective sensory testing.

These methods of odor testing do not easily allow these comparisons over location and time (Miner & Licht, 1981, Miner et al., 1995) due to difficulties in sampling for laboratory analysis, in maintaining the consistency of testing conditions for on-site testing methods, and to variations in the methods for sensory analysis. Laboratory methods such as the Dynamic Dilution Method require the on-site sampling in a 50- or 60-litre Tedlar (polyvinyl fluoride) plastic bag and its transport to the laboratory in a rigid, airtight plastic drum. The scentometer, a device for field testing, allows the on-site evaluation of increasing concentrations of the odorous air and has received wide use in earlier malodor testing. Among the problems reported for this method are odor fatigue, which diminishes the sensitivity of the observer, and the instrumental difficulties of the saturation of the charcoal bed that is part of the air filtration system. Other problems with this method include the degree of training of the observer and the ability of the observer to handle and

recover from odorant exposure, and the lack of capability to compare treatments and locations directly (Miner & Licht, 1981).

Various systems have been devised for the presentation and sensory assessment of odorants. In the past these have all been systems for the delivery of the odorant stimulus to the human assessors under controlled conditions. More recently odor assessment has included a completely new technology based on the use of sensor arrays of either conducting-polymer or metallic-oxide sensors connected to neural networks and known collectively as electronic-nose technology.

2.2.1 Olfactometry Applied to Environmental Malodors

Generically, an olfactometer is any instrument designed to control and manipulate the concentration of odorants that are delivered to assessors for evaluation as required by a given test procedure. They have been used both in the study of odorant thresholds and in suprathreshold odors (Engen, 1982). Several olfactometers have supplied odorant stimuli in most olfactory research. These include the dynamic dilution olfactometer, the Scentometer®, the Odorometer®, and the Nasal Rangers®.

The dynamic dilution olfactometer is a device for presenting accurately measured quantities of an odorant, in terms of both quality and intensity. It presents the assessor with a constant gentle flow of vapor whose rate closely matches that of normal breathing and whose temperature is close to body temperature. The sample is obtained by first saturating the odorant (the field sample) with a carrier gas (purified, odorless air). It is carried through one channel into a mixing chamber into which the same purified air can be added at controlled rates through another channel. This mixing allows the dilution of the field sample and controls its concentration. The specified concentration of odorant is delivered to the assessor through an aperture and the required assessments made according to the test design. The system provides forced choice test. The system which is sold by St. Croix Sensory, Inc. uses a 3-alternative

forced choice presentation of 2 carrier gas samples/1 odorant sample, referred to as a triangular presentation in this context. This test method is described by Chen et al. (1999) and Zhang et al. (2002). This method relies on odor measurement by human assessors who must be selected and trained appropriately for the tests. This method can be used with on-site sampling of odorous air in large Tedlar® bags that provide the initial sample for assessment and dilution as described above. International standards have been developed for the use of this measurement system (CEN, 1999).

The Scentometer® is a portable device that is used for intensity measurement of odors in the field. The user inhales through two nasal inserts (one for each nostril) through which odor-free air (channeled through an activated charcoal filter) is presented. Then multiple odorous-air inlets of various diameters are used, beginning with the lowest amount, to introduce the odorant. The odor is measured as the dilution at which it is first detected. The difficulties of this test include assessor fatigue; problems with complete “rinsing” between samples (i.e., the return to the baseline condition of the odor receptors in the nose between observations), and the potential for the saturation of the activated charcoal with the odorants resulting in the presentation of contaminated “reference” air to the assessor and the suppression of accurate odor perception (Miner & Licht, 1981). The Odorometer® is another portable device for use in field testing malodors with sensory panelists. Its use is described by Schiffman et al. (2001).

Nasal Rangers® describes a group of trained assessors who work in a field situation. This particular name is under copyright to St. Croix Sensory, Inc. In application (including work at the University of Manitoba), this is used for the data collection portion of odor dispersion studies. It uses magnitude matching of a perceived odor strength to a geometric scale of 1-butanol concentrations. One format uses 15 assessors placed in a particular pattern downwind of an odor source and required a sensory assessment of odor every 10 s for 3-10 min periods over a 1-h session. Assessors are equipped with a facemask/activated charcoal filter that supplies clean air between evaluations. This allows “rinsing” and re-zeroing of the odor receptors. This is

generally followed by testing with a dynamic dilution olfactometer to further standardize the odor source for the modelling system. (St. Croix Sensory, Inc., 2000; Zhang, 2003, personal communication).

2.2.2 The Complexity of the Malodor Stimulus

The study of malodors is made more complex by the nature of the stimulus – usually a mixture of many compounds that are produced by both production and breakdown of the source material. This is particularly apparent in work on malodors from swine production. Several workers discuss this and have shown the large number and variety of compounds that are present in either the waste products themselves or in the atmosphere around them. Spoelstra (1980) identified 150 volatile compounds in waste from “piggery wastes” and proposed the use of *p*-cresol and volatile fatty acids as indicators of odor intensity. Persaud et al. ((1996) used GC/MS analysis to evaluate pig slurry (fresh manure) and identified 10 manor components plus ammonia to formulate an artificial pig slurry. Zahn et al. (1997, 2002a, 2001b) evaluated the composition of airborne malodors from swine operations and attempted to characterize these facilities through the composition based on specific components. From over 200 compounds identified over all samplings, they identified 20 which were present in all samplings and based a synthetic swine odor mixture on these compounds. O'Neill & Phillips (1992) reviewed literature on livestock in general and reported references to 168 different compounds associated with livestock buildings. Schiffman et al. (2001) quantified 331 different VOC's from swine-holding operations in North Carolina, including acids, alcohols, aldehydes, amides, amines, aromatics, esters, ethers, fixed gases (NH₃, CO₂, CO, and SO₂), halogenated hydrocarbons, hydrocarbons, ketones, nitriles, other nitrogen-containing compounds, phenols, sulfur-containing compounds, 8 steroid-like compounds and 16 unclassified compounds.

2.2.3 Artificial Swine Odors – or Swine Odor Simulants

The production of an artificial hog odor, a “swine odor simulant”, facilitates some types of work in studying these malodors. Table 2.1 shows the concentrations of two simulant mixtures that allow a standardized odor source of swine odor for laboratory use. Persaud et al. (1996) developed a mixture based on 11 compounds and without any sulfur-containing compounds, due to the safety factors associated with using these chemicals. This mixture was used to evaluate the performance of an electronic nose system with conducting polymer-based sensors. Later work by Zahn et al. (2001) showed a mixture of 21 compounds including sulfur-containing compounds for work with odor characterization that had been identified in their earlier work (Zahn et al., 1997). For both of these mixtures, the individual compounds do not smell like manure, but the combinations have the definite aroma of the emissions of hog barns and lagoons.

Table 2.1. Composition of swine odor mixtures proposed as simulants based on chemical composition of malodor emissions from swine operations.		
Component	Persaud et al. (1996) ppm	Zahn et al. (2001) mM
acetic acid	1365	8
propanoic acid (propionic acid)	358	3.5
2-methyl propanoic acid (isobutyric acid)	604	0.5
butanoic acid (n-butyric acid)	237	1.4
3-methyl butanoic acid (isovaleric acid)	301	0.2
pentanoic acid (n-valeric acid)	90	0.5
phenol	21	0.15
4-methyl phenol (p-cresol)	62	0.2
indole	6.6	0.1
3-methyl indole (skatole)	3.7	0.15
ammonium hydroxide (NH ₄ OH) 5%stock solution	adjust to pH 8.2	
dimethyl sulfide		0.05
2-butanol		0.4
isocaproic acid		0.1
caproic acid		0.2
heptanoic acid		0.2
4-ethyl phenol		0.12
benzyl alcohol		0.1
2-aminoacetophenone		0.15

butylated hydroxytoluene (preservative)		0.1
ammonium acetate		8
potassium hydroxide – 2M		adjust to pH 7.0

2.2.4 Applications of Scaling to the Sensory Analysis of Environmental Malodors

Various studies on swine odor have used different approaches through sensory methodologies. The 1-butanol scale, for magnitude matching measurements of odor intensity is commonly used for this purpose (CEN, 1999). This particular scale is used as an international standard for the measurement of odorant intensity in dynamic dilution olfactometry of malodors. Magnitude estimation has been applied to evaluate the effects of synergy from various odor components on the overall swine odor. Zahn et al. (2001) used magnitude estimation to measure the constant of Stevens' Law for a synthetic swine odor mixture (Table 2.1). They used five dilutions of the stock solution and 14 panelists to generate the values for the formula. They also studied certain mixtures of components for synergisms and antagonisms between these components. The slope of the best-fit line was found to be $b = 0.265$, and this was compared to solutions that were supplemented with some of the individual compounds. The solutions with two-fold concentrations of specific components showed increased values for the exponent, indicating a change in the perception of these solutions. The newer scaling method for ratio data, the Labelled Magnitude Scale, has been used Zhang et al. (1999) to evaluate the intensity of cotton flannel swatches exposed to odors from hog slurry in a controlled exposure system, as part of the development of this method of testing the effectiveness of odor treatments.

2.2.5 Quality versus Quantity in Odor Assessment

An aspect of odor assessment that is often included in the work on malodors is a measurement of "pleasant versus unpleasant", which, because of the actual physical reaction that human beings have to these types of malodors, is different from what is thought of as hedonic testing. As was previously discussed, there is a common cross-cultural response to waste product odors that can make this assessment analytic rather than like-dislike. The aspect of unpleasantness

leads to another area of odor measurement that is odor annoyance. Workers such as Lidén et al. (1998) have evaluated this a psychophysical function that can be used with Stevens' Law to calculate the exponents for annoyance as well as intensity.

Another aspect of odor quality is the description of the sensation the odorant induces in the perceiver (the odor quality). This is dependent on the concentration of the stimulus, with the description changing with increasing concentration. Doty (1975) showed the relationship of concentration, intensity and pleasantness in a series of odorants, with the characterization of pleasantness being associated with different intensities for different odorants. Gross-Isserhoff and Lancet (1988) evaluated the qualitative changes in 14 odorants with changes in concentration. Another example of this phenomenon is that low levels of amyl acetate are described as "apricot", high levels are "putrid". Zahn et al. (2001) reported the concentration-dependent descriptors of their artificial swine odor. The odor descriptors change from 1% characterized by barely detectable, very milky, sweet smelling, and slightly/moderately unpleasant to 50% characterized by unpleasant, wet socks, foot odor, slightly bothersome and rotting garbage, to 100% including descriptors of very bad, powerful, very unpleasant, ammonia, and sickening, with four other intermediate concentrations included. While these descriptors were generated by a panel that was not trained for descriptive analysis and are thus essentially naïve in descriptive panel work, the descriptors create a clear continuum.

2.3 Odor Adsorption by Different Fabrics – Evaluations from Textile Testing

2.3.1 Fabric Swatch Measurements of Agricultural Malodors

Observations on the uptake of odors on cloth swatches have been reported since the 1980s and developed from observations of the common phenomenon that livestock manure odors adhered to clothing worn while working in the animal- and waste-handling environments for some period of time. Fabric swatch methods have been described in the literature on malodor assessment. Indole and skatole, two odorants associated with strong faecal odors, are reported as

being characterized by their stability on cloth for extended periods of time (Miner & Licht, 1981). Swatches of cotton and wool flannel were tested initially by suspending them in the test areas for varying periods of time, and cotton flannel was selected for use in further testing based on these preliminary results. This fabric has continued to be used in current applications of the test method, although no source or specifications are cited for the fabric used.

This stabilization of the odors began to be explored to a limited degree as a pathway to transport the odors to another location for sensory analysis. Several authors have used exposure of cloth swatches to stabilize odors for transport to a laboratory for further analysis (Labance et al., 1999; Nicolai et al., 1997; Williams & Schiffman, 1995; and Miner & Licht, 1981). Various types of standardization and presentation have been reported including placing of swatches of specified sizes within barns and at air outlets for controlled amounts of time however, the exposure was relatively unregulated and depended on the conditions present in the environment and any other variables introduced through this pathway that were not accounted for in the testing. After exposure the swatches have been placed into containers such as glass jars, Tedlar bags and plastic bags to stabilize them for presentation to sensory panelists for responses to measure the strength of the odor. The cloth has generally been cotton flannel; while one study used wool flannel as well. The fabric sources and condition have not been specified. Generally the size of swatch used is given, but not the source of the material and the degree of pretreatment given the samples. The assumption must be made that the fabric was obtained from fabric shops and was likely treated with dyes and other standard finishes. Washing the fabric is cited as a preparation method in some references.

The test was not approached as a possible standard test until a method of exposing the fabric swatches under standard test conditions was developed by the Department of Biosystems Engineering, University of Manitoba. Through the use of controlled airflow sampling, the fabric can be exposed to air-borne odorants and the sample stabilized by containment for laboratory evaluation under controlled conditions in a sensory testing laboratory. Initial work on the

controlled exposure of cloth swatches (cotton flannel) to manure malodors has been reported by Zhang et al., (1999). This work presented the evaluation of cloth swatches that had been exposed to specified volumes of air for specific time periods and showed the successful objective sensory measurement of the uptake of the odorant onto the fabrics. The current work on a standardized swatch test is designed to provide simpler sampling procedures that are less cumbersome and expensive. It can provide greater test flexibility in the format of the sensory analysis methodology that can be used and allow the comparison of results within and across testing.

Schiffman et al. (2001) described using cotton flannel swatches that were deodorized with methylene chloride and purged in nitrogen and then in a vacuum oven to remove the solvent. The swatches were placed in glass tubes and varying quantities of air inside swine houses was pulled through the samples using a Gilair-5® pump system. The cotton flannel swatches were found to collect essentially the same volatiles as Tenax® sampling cartridges, and both provided enough of the odorants for similar results from GC/MS. The observation is made that “the collection and concentration of odorous air onto adsorbents off-site needs further development to provide for quantification when odor is intermittent”(p. 237).

2.3.2 Cloth as a Substrate for Odor Adsorption

The successful application of the swatch-method for testing of air-borne odors is dependent on the properties of the fabric chosen to be the carrier or stabilizer for the odorants. The fabric selection and usage in this test to date has been based on observations of odor presence on garments of unspecified construction and on very limited work with two types of flannel (cotton and wool), that dealt only with the barn exposure of pieces of fabric for periods of time and comparisons of the resulting adhering odors.

The role of textiles in this sampling system is, of course, pivotal, so some consideration needs to be given to the nature of the substrate for this final sampling process. Cloth, the substrate, is made up of fibres that may be spun into yarn and then woven into cloth or that may

be formed into a web and stabilized as a non-woven textile. Fibres are made up of polymers, large linear molecules with particular structures and groups on the surface of the molecule that determine the nature of the surface. In this work, we are dealing mainly with the outer surface only as the bonding of the molecules would be expected to be only those of the top layer.

The amount of absorptive surface that is available for odor adsorption depends on the structure of the cloth, the way in that the yarn from that it is woven was spun. Basically the amount of absorptive surface is related to factors such as the surface area of the fibres from which the yarn is spun minus all of the contact areas between fibres and yarns within the fabric. This can be described by factors that can be measured, such as porosity, which is defined in ASTM D 4850-99. Porosity is the ratio of the volume of air or void contained within the boundaries of a material to the total volume (solid matter plus air or void) expressed as a percentage.

$$\text{Porosity} = (V/T) \times 100$$

Where: V = volume of voids, and T = total volume (Guidon et al., 1987)

The surface, for the purpose of surface analysis, is described by Vickerman (1997) as being considered in three forms or regimes:

1. the top surface mono-layer – the surface atoms that are the immediate interface with the other phases impinging on it.
2. the first 10 or so layers – the atoms immediately below, that significantly determine the structure and chemistry of the top layer and is approximately 0.5 to 3 nm.
3. the surface film, no greater than 100 nm.

Beyond 100 nm, he describes it as being considered as the bulk solid state properties.

It is expected that the surface chemistry of such fabrics is likely to play an important role in the adsorption/desorption of odorant molecules. Techniques such as Fourier transform infrared (FTIR) spectroscopy with attenuated total reflectance (ATR), electron spectroscopy for chemical analysis (ESCA), and contact angle measurements to determine the hydrophilic/hydrophobic character can be used to characterize the surface of fabric swatches. In addition, attempts to

visualize the adsorption of olfactory molecules on the fabric substrate will be undertaken by imaging the electron density of the fibre surfaces by scanning tunneling microscopy (STM) and/or atomic force microscopy (AFM) before and after exposure (Ratner, 1996). The equipment to perform these analytical tests is available at either the University of Manitoba or the Quebec Biomaterials Institute, Laval University. The selection of a system to provide the desired information is based on two factors, the availability of technology, and the scope of the information that can be generated by a system, i.e., if one system will give more than one type of information which is needed, then it becomes more useful for data collection.

2.3.3 Requirements for Surface Analysis Methods Applied to Biomaterials

Some of the most important characteristics for any of the methods that might be used in conjunction with the other analyses to examine the surface of cloth swatches for collection of odor samples are as follows (Ratner, 1966):

1. sample stability in preparation. This characteristic echoes Ratner's (1996) concern that "in sample preparation the sample should resemble, as closely as possible, the material or device being subjected to biological testing or implantation" (p. 22).
2. knowing the way in which the surface might be damaged . In surface analysis, the method of analysis may alter the surface.
3. sample "noise" as an artifact of surface damage. This characteristic underscores the desirability of more than only one sampling method to disentangle the "real" sample from the sample plus noise.
4. differences in susceptibility to surface damage among different materials for obtaining samples. Organic and polymeric materials are more easily damaged by surface analysis than are the materials the methods were developed using, i.e., metals, ceramics, glasses, and carbons.

5. differences in surface mobility among different sampling systems. For example, polymeric systems exhibit greater surface mobility than inorganic systems.

Another consideration in the use of these methods is that the beam is focussed through a vacuum, so that air molecules will not deflect it or otherwise interfere with the readings. These methods were used to analyze stable features of the cloth surface, but not adsorbed odors as they are weakly bonded and would be removed when placed in a vacuum. The surface chemistry of the fabric is expected to be one of the most important areas to explore in this research as the chemical structure in the top 100 nm of the fabric is not the same as the remainder or bulk of the material (Ratner, 1996).

2.3.4 The Importance of the Nature of the Fabric Swatch to the Success of the Test

Currently, little information is available in the sensory literature regarding the relationship of the type of textile used on the adsorption and desorption of odors from fabrics. There is also no information on the effects of finishes or finishing methods on odor uptake and release or on the inherent odors of different fibres/fabrics. One study deals with the functional properties and inherent odor attributes of commercial cat litter manufactured from various base materials including alfalfa and clay (Cliff & Heymann, 1991) related to several physical attributes including particle size, density, pH and water holding capacity. Of those tested, the cellulose-based product from alfalfa had the best odor control.

Textile analysis of the commercially available standard fabrics included a number of approaches. The type of textile structure, whether knitted, woven, pile, napped, etc. used in the standard fabrics was identified. In addition the physical characteristics of these fabrics were characterized in terms of fabric counts, air permeability (the rate of airflow through a material under a differential pressure between the two fabric surfaces), fabric weight, fabric thickness and fabric porosity (the ratio of the volume of air or void contained within the boundaries of a material to the total volume, (solid matter plus air or void) expressed as a percentage). These are

all defined by standard test methods from the American Society for Testing and Materials and the American Association of Textile Chemists and Colorists.

Liu et al. (2004) discussed their study using electron microscopy and x-ray microanalysis were used to evaluate the distribution of an odorant (*cis*-3-hexenyl salicylate) which was tagged with osmium tetroxide. The study was done using dyer's methodology, i.e., wet application of the test substance to the textiles. Three fabrics were used as 5-cm diameter swatches. These were cotton print cloth #400, and Dacron type 54, #777 from Testfabrics, Inc., and lyocell (Tencel® chambray). Each was exposed to an aliquot of the test odorant followed by exposure to osmium tetroxide vapor for several hours. Microscopic analysis showed that the odorant was distributed differently on the different fibres and was "correlated strongly with the chemical structure, roughness and both pore and capillary structure of the textiles" (p.3557). Cotton fibres are rough and irregular and have the appearance of a collapsed tube with micropores and interfibrillar spaces large enough for the odor chemical to penetrate. The odorant was found through "the whole cotton fiber cross section with higher concentrations in lumen and crenulations" (p.3557). Lyocell is the same chemical composition as cotton but has no lumen, is round and has a microfibrillar structure with three phases (crystalline, larger air-filled voids and smaller-defect regions). They found that the odorant was distributed evenly in the surface and cross section of the fibres. Dacron (or polyester) is formed from polyethylene terephthalate, is melt-spun, and has very few or no voids. The odorant was found at a few spots on the fiber surface and in interfiber spaces of closely packed fibers.

2.3.5 Commercial Products Which Exploit Odor Technology

An interesting side-note is the recent introduction of commercial products based on odor adsorption and release properties. This leads to the speculation that much information on odor technology is available, however, under proprietary circumstances only. Two of the different products in the marketplace that deal with odor adsorption for control are the Scent-Lok® line of

clothing and Febreze®, a liquid product which is sprayed on cloth for the elimination of odors from that surface. Scent-Lok® clothing is used by hunters to reduce their scent while they are out in the field. The product is based on activated carbon cloth as part of its construction and is accompanied by laundering and storage instructions for regeneration and stability. Febreze® liquid is another interesting product that really does help reduce the odor level on cloth. The composition of the product is proprietary, but one speculation is that it changes the surface chemistry of the fabric to cause the temporary hydrogen bonds to break and to release the odor more easily.

2.3.6 Odor Substantivity on Textiles – the Concept and How it Applies in our Testing

An important consideration in using textiles as an odor sampling medium is the stability of the sample both for integrity and for time. Substantivity is a term used in several fields to mean a product's time-dependent condition relative to its original condition. In terms of perfume, Ormancey et al.(2000) defined it as “the amount of time a perfume remains perceptible on a support” (p. 24). In dentistry it is used with the evaluation of products, such as tooth whiteners and oral treatments for gingivitis, remaining in place for a given period of time. It is similarly used in dermatology for the degree to which a product applied to the skin, such as a sunscreen, remains in place and active.

The studies on substantivity contain information on the nature of the fragrance and the measurement of its level in the application at different points in time. However, these studies have focused more on the form in which the odorant is added to a given cloth substrate (nature of the solution) rather than how it reacts with different fabrics. Müller et al. (1993) discussed “substantivity” relative to fragrances in terms of the measurements used to evaluate it in various liquid and solid agents. They defined it as a quantitative determination of the odorant's time dependant-concentration above the perfumed product. Measurements included vapor pressure, odor perception threshold (using on olfactometer), water solubility and matrix factors (the liquid

or solid in which the odorant is dispersed). These measurement methods have also been discussed by Gygax & Koch (2001). Additionally substantivity of perfumes has been monitored by electronic noses. Moy et al. (1994) briefly discussed their use of an early model Alpha MOS Fox 2000 in evaluating perfume stability on washed towels, indicating that they were successful but supplying no data. Ormancey et al. (2000) evaluated the effects of raw material changes on substantivity in standardized laundry testing, in this case to wet, dry and re-wetted terry cloth. They used an electronic nose to compare the results from the raw materials and were able to follow the changes in specific components with specific sensors.

From the perfumer's point of view, substantivity is an operational characteristic and a fragrance or odorant is substantive when it is perceptible throughout the stages of a product's application cycle. Table 2.2 is an example of the requirements for scents used in fabric softeners. These requirements are used to formulate some desirable attributes for cloth swatches which would be used in environmental malodor sampling.

Table 2.2 Equating some requirements for substantivity in cloth swatch testing to requirements for substantivity in fabric softeners (based on Ormancey et al., 2000).	
Requirements for fabric softeners:	Attributes necessary for cloth swatches in order to apply to environmental testing:
Olfactory sensitivity that is sufficient to be perceptible.	Capable of adsorbing an odorant level which is sufficient to form a representative sample of the environmental situation.
A pleasant fragrance that is coherent with the notions of softness, cleanness and freshness.	That the odor is representative of the environmental situation, i.e. both by character and intensity (and usually unpleasant).
A fragrance that is substantive enough to remain perceptible on the cloth for several days or weeks.	That the sample retain the odor for a sufficient amount of time to be transported and analyzed – preferably several days.

In work with the sampling of malodors onto fabric, it will be used in conjunction with the time-dependent delectability and concentration of odorants on the fabric's surface.

2.4 Chemical Methods for Odor Headspace Analysis

It is believed that the surface chemistry of fabrics is likely to play an important role in the adsorption/desorption of odorant molecules. An important aspect of this chemistry is the hydrophilic or hydrophobic properties of the surface. Techniques such as Fourier transform infrared (FTIR) spectroscopy with attenuated total reflectance (ATR), electron spectroscopy for chemical analysis (ESCA) and contact angle measurements are used to determine hydrophilic/hydrophobic character of a fabric (Ratner, 1966). There are also methods such as imaging the electron density of the fibre surfaces by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) before and after exposure (Ratner, 1996), which can be used to visualize the adsorption of olfactory molecules on the fabric substrate.

New techniques applied in textile production, such as ion beam and plasma etching, corona discharge and UV irradiation, which can be used to change the surface topography of fibres and, hence, increase the total surface area available for odorant adsorption (Ratner & Hoffman, 1996). Hwang (2003) has demonstrated this type of application with the applications of plasma polymerization to alter the nature of the textile surface for specific functions.

One of the methods of analysis of surface chemistry – ESCA/XPS (electron analysis for chemical analysis/X-ray photoelectron spectroscopy) provides a way to evaluate the surface of the product (here, textile)(Ratner, 1996). Vickerman (1997) described the basic principle of the method as “X-ray photons of precisely defined energy bombard the surface, electrons are emitted from the orbitals of the component atoms, electron kinetic energies are measured, their electron binding energies can be determined enabling the component atoms to be determined” (p.4). Ratner (1996) described the method as “X-rays are focused upon a specimen. The interaction of the X-rays with the atoms in the specimen causes the emission of a core level (inner shell) electron. The energy of this electron is measured and its value provides information about the nature and environment of the atom from which it came” (p.23).

Ratner (1996) further stated that the method measures the outermost 100 Å of a surface. Although the electron beam can penetrate deeply into a specimen, the electrons from those layers will lose their energy by collisions before they ever get to the surface, so will not emerge from the surface. Only those at or near the surface will be emitted and gathered in the signal. The method is readily applicable to biomaterials and, hence, to textiles. The surface structure can vary widely from a surface that is rough, smooth or stepped, that is composed of different chemistries (atoms and molecules), that is structurally or compositionally inhomogeneous in the plane of the surface and with the depth into the specimen, that is covered by an over-layer, or that is highly crystalline or disordered. In other words, it will work on almost any surface.

Advantages of the method include the speed of analysis, the high information content, the low damage potential (it is a non-destructive method), and the absence of specimen preparation. Its disadvantages are that the sample must be able to be placed in a vacuum – no out-gassing of volatile components, although this disadvantage can be avoided by using a system with a cryogenic sample stage. At liquid nitrogen temperatures, samples with volatile components and wet samples can be analyzed. Sample damage is possible if long analysis times are used. Experienced operators should run the equipment. This method yields information on both chemical composition and chemical structure (Vickerman, 1997). Ratner (1996) expands on this with the following list for analyses of biomaterials:

1. Identification of all elements (except H and He) present at concentrations of > 0.1 atomic %,
2. Semi-quantitative determination of the approximate elemental surface composition ($\pm 10\%$),
3. Information about the molecular environment (oxidation state, bonding atoms, etc.),
4. Information about aromatic or unsaturated structures from shake-up transmissions,
5. Identification of organic groups using derivatization reactions,
6. Non-destructive elemental depth profiles 100 Å into the sample and surface heterogeneity assessment using angular-dependent ESCA studies and photoelectrons with differing escape depths,

7. Lateral variations in surface composition (spatial resolution is 8 to 150 μm depending on the instrument used),
8. “Fingerprinting” of materials using valence band spectra and identification of bonding orbitals,
9. Studies on hydrated (frozen) surfaces.

A method of changing the surface chemistry of textiles is through a process called plasma polymerization. It is based on the use of plasma – “an ionized gas in a neutral state with an equal density of positive and negative charges – also called the fourth state of matter” (Hwang, 2003, p. 1). Through the exposure of a surface to a plasma in an appropriate environment, the surface can be modified by the components of the plasma. This is used in industries such as electronic parts, lighting and large-screen televisions and novel finishing techniques for textiles. One of the attractions of the process is that it is a dry process and, therefore, does not require the production of waste-water, which is an expensive part of textile processing (Hwang, 2003).

2.5 Electronic-Nose Technology in Environmental Testing

2.5.1 Electronic Nose Technology

Electronic nose technology for the measurement and comparison of difference product groups by their odorant properties is a new development (over the last 10 to 15 years). The technology uses the electronic signal pattern generated within sensor arrays, which adsorb odorants and release them in a manner conceptually similar to the human nose, to characterize and categorize particular products. With the addition of neural networks, these machines have developed into measurement systems that can evaluate many different product states (e.g., deteriorative changes within a product) and are particularly suited to the measurements of malodors in both food and non-food products (Schiffman et al., 1997).

In this way, the electronic nose is one type of expert system, which can be applied to predict human assessments. Expert systems are described by McLellan (1989) as being

“knowledge-based programs that emulate expert thought to solve significant problems in a very specific domain of expertise” (p. 120). Risvik et al. (1989) discussed one of the problems “at this point in time”, in sensory evaluation as being the lack of a sufficient number of sensory professionals with the knowledge and experience of the full range of applications in the field of sensory science. A knowledge-based computer system could form the guidelines for all stages of design and analysis for sensory studies.

This problem extends into the area of the sensory assessors who perform the judgements on samples. Persons must form the assessment base of all product assessments that do not have implications for human health and safety. This means that the attributes and acceptability of all products require human input for the product attributes and the appropriateness of these attributes for buying behavior. Sensory analysis can be thought of as a system for product assessment with economic implications.

An electronic nose consists of three basic parts, a sample delivery system, a set of sensors and a computer. The sample delivery system for holds samples under specific conditions and prepares them for presentation to the sensors. In the Alpha MOS system, this is a multi-use auto-sampler from another manufacturer (commonly used for instruments such as gas chromatographs) where exact volume control and handling conditions are essential for analysis. Other systems have also developed auto-sampler systems, which have made the systems useful in ongoing laboratory analyses; whereas, early systems required single sample presentation and the constant presence of lab personnel to monitor the instruments. The set of sensors responds to the presence of odor components by a change in the response of each sensor, and this change becomes the data for analysis. In the Alpha MOS instruments, these sensors are based on metal oxide coatings, and the response is a change in electrical resistance of the metal oxide coating. Other types include conducting polymer sensors (change in electrical resistance), quartz crystal microbalance sensors (change of frequency), and a combination known as GC/SAW or gas chromatography/surface acoustic wave system. This latter is actually more of a gas chromatograph with one SAW sensor

that responds to the chemicals that have been passed through a chromatography column and are tested in sequence depending on their retention time in the column. The computer with custom designed software, receives the sample codes for a given sample set and accumulates and stores the electronic patterns for each sample analyzed. These data points for the electronic patterns form the machine data for analysis of the samples. Specific software may contain data analysis routines as well, or data may be stored in spreadsheets for analysis in programs such as SAS and SPSS. The high capacity for data handling and analysis of the desktop PC is perhaps the single most significant advancement that has made the electronic nose useful in the laboratory. While the instruments and sensors have been under development since the 1980s, their use did not spread widely until the late 1990s when lab analyses became practical.

The practical side of electronic nose analyses is that each of these basic parts has specific protocols, which must be developed and observed for the functioning of the instrument and for the collection of reliable and representative data. Some of these are universal in the concept of experimental design, and some are specific to specific machines or to specific sensors. In addition, within any given system, some are constant across projects, and some are conditions that must be optimized for each commodity and/or study. Beyond this, any study requires protocols for strategizing the relationships between sensory and electronic nose evaluations of specific sample sources.

The sensor array of the electronic nose is connected to a computer, which allows the pattern of responses to be identified. Through standardization, compared to human responses, the system can be “trained” through its neural network to identify specific odor conditions (e.g., the presence of odors that indicate decomposition in specific food products or the presence of odors in wounds that indicate the beginnings of infection). In some instances this technology has been applied to the evaluation of odors from livestock operations. These machines are standardized prior to use by comparison to human sensory responses to the specific odorant conditions and,

thus, do not involve the use of sensory panels in their day-to-day operation. (Alpha SOFT User Manual, June, 2001)

2.5.2 Applications of Electronic Nose Technology to Textiles and Environmental Testing

There are literally hundreds of references on the applications of electronic nose technology in various industries including food processing and inspection, medicine, environmental testing and textile and automotive production. In applications to textiles electronic nose systems have measured the odor properties of automotive textiles, both leather and upholstery materials and padding (Garrigues et al., 2001; Kalvan et al., 2000; Morvan et al., 2000). In application to environmental testing, electronic nose technology has characterized of environmental malodors from a variety of industrial and agricultural sources (Persaud et al., 1996; Classen, et al., 1997 & 2000; Maricou et al., 1998; Romain et al., 2000; Nicolas et al., 2000). In all cases the sampling used gaseous samples taken from Tedlar®, or similar, sampling bags. Persaud et al. (1996) used an artificial swine odor mixture to evaluate a conducting polymer array for its ability to distinguish malodor sources. Romain et al. (2000) used a simple tin oxide sensor system to establish that differences in emissions from five locations – a rendering plant, a sewage treatment facility, two printing houses, and a car repair facility. Nicolas et al. (2000) used the same system to evaluate seven different facilities to classify malodors.

In its use as an expert system, the electronic nose has a large range of potential applications: from objective designation or description of scent for trademark (Breese, 1998), to clinical diagnosis in medical applications (Pavlou & Turner, 2000), to process control in the food industry (Linko, 1998). Part of the system is an appropriate neural network, so that the combination of the knowledge-based (expert) system and the artificial neural network offer great potential.

Chapter 3

Study #1: Evaluation of Two Ratio Scaling Methods Using a Standard 1-Butanol Scale and the Electronic Nose

3.1 Introduction

A variety of scaling systems, both linear and ratio, have been used in evaluations of taints and malodors. These include “direct” systems such as difference-from-control and various linear scales in which the intensity was rated based on the stimulus alone and the anchor points of the scale presented. Another system was a form of magnitude matching using a reference scale that was learned and then used in describing the intensity of the sample stimulus in terms of the intensity of the samples in the reference scale. When these scales were designed, they were generally in the form of concentrations that increased by a multiple (e.g. doubling) so that the scale was ratio in nature. One of the most common scales was based on concentrations of 1-butanol described by ASTM E544-99 and another of different concentrations used by St. Croix Sensory, Inc. as part of their proprietary “Nasal Ranger” system for environmental monitoring.

In the current study, the labelled magnitude scale was selected for both its ease of administration and resulting “ratio” data. The labelled magnitude scale was a pen and paper method of ratio measurement, which was easier to use and supplied the same information as traditional magnitude estimation. Because the intention was to use this method in the sensory measurement of malodor on cloth swatches, some initial evaluation was in order. One way of examining it was comparing one of the scales to be used in a subsequent study, the 1-butanol scale from ASTM E544-99. This involved selecting and training a panel comparable to the group that would be used in succeeding studies for laboratory analyses of malodors on fabrics and for field studies of malodor.

3.1.1 Objectives and Hypotheses

This study had three objectives. The first objective was to evaluate the use of the labelled magnitude scale relative to magnitude estimation in the measurement of sensory intensities for 1-

butanol, a compound commonly used in environmental malodor testing as a standard for magnitude matching. Both scales produce ratio data, which means that these data could be compared by calculating the exponent for Stevens' Power Law. The second objective was to evaluate the electronic nose sensor responses to discriminate among the concentrations in the series of 1-butanol solutions used for sensory analysis. The third objective was to compare the sensory and electronic nose responses to the 1-butanol concentrations.

Hypothesis I: The hypothesis being tested was that the value of the slope (n) of the line relating the log of perceived intensity to the log of physical intensity (concentration) for 1-butanol solutions from Stevens' Power Law ($\log S = \log k + n \log I$, see Section 2.1.3) is equivalent for both the labelled magnitude scale and magnitude estimation.

Hypothesis II: The hypothesis being tested was that the discrimination index value from principal component analysis for the electronic nose sensor responses to the 1-butanol concentrations was equal to or greater than 80% (see Table 1.2).

Hypothesis III: The hypothesis being tested was that sensory scores for the 1-butanol concentrations correlate with the electronic nose sensor responses for those samples.

3.2 Experiment 1. Sensory Analyses

3.2.1 Introduction to Experiment 1

The purpose of the first study was to compare the use of the labelled magnitude scale and magnitude estimation in the sensory testing of a series of 1-butanol solutions based on ASTM E544-99 as a basis for work in subsequent studies. The hypothesis was that the data from the labelled magnitude scale would provide the same result for the calculation of the exponent of Stevens' power law as the data from magnitude estimation. The series of solutions and the sensory data was also used to evaluate the performance of the electronic nose system, which

would be used in subsequent work (discussed in Part B of this section). This analysis was done through linear regression subroutines in the data analysis software.

3.2.2 Methods and Materials:

Several steps comprised the first study:

1. establishing an appropriate scale to be used for the work,
2. selecting a group of panelists who were able to perceive and differentiate small differences in concentrations of 1-butanol, the selected test odorant using a sequential testing method developed for taint analysis,
3. training the selected panelists to the basic procedures for the two scaling methods, and
4. evaluating a large scale range of log-spaced 1-butanol concentrations (5 to 20,000 ppm).

3.2.2.1 1-Butanol Solutions

The concentrations were selected based on the information in ASTM E-544-99 (American Society for Testing and Materials, 1999) and are shown in Table 3.1. All solutions were prepared using the "Procedure B in Section 6 - the Static Scale Method" of ASTM E-544-99 using 1-butanol (Certified A.C.S, 99.8%, Fisher Scientific, Ltd.) and odorless distilled water from the laboratory supply system at the Freshwater Institute, Winnipeg. The very lowest concentration of 5 ppm in solution was used in this study, even though it was considered to be sub-threshold, to provide a sample that was low but not zero to evaluate the performance of the panel (and the electronic nose). The maximum useful concentration was 20,000 ppm, above which odor was reported as being too intense for most comparisons.

Table 3.1 Concentrations of 1-butanol used based on ASTM E-544-99.

Concentration in water ppm	Concentration in air ^a ppm (est.)	Code for Electronic Nose Maps and Graphs
5 ^b	0.5	L01
10	1	L02
25	2.5	L03
50	5	L04
100	10	L05
250	25	L06
500	50	L07
1000	100	L08
2500	250	L09
5000	500	L10
10000	1000	L11
20000	2000	L12

^a calculation based on St. Croix Odor Intensity Referencing Scale information and on Cometto-Muñiz et al. (2003).

^b this concentration is below the recommended starting point of 10 ppm in water and should be below threshold.

3.2.2.2 Sensory Panel Methodology

3.2.2.2.1 Panel Recruitment and Selection

The panel was selected from employees at the Freshwater Institute and the Department of Biosystems Engineering, University of Manitoba. Potential panelists were asked several basic questions regarding interest and availability for this work as well as their general health and ability to perceive common odors. They were informed about the nature of the work and the samples both verbally and through the informational letter and consent forms, shown in Appendix A. All panelists were required to sign the “Informed Consent” form in order to participate in the studies. Candidate panelists were required to have no respiratory problems and be able to pass the selection test for the ability to perceive and quantify the presence of 1-butanol. The aim was to have a group of 15 to 20 panelists who would be available for both studies so that, allowing for normal panel attrition over the time period, a final set of at least 10 panelists would complete the

sessions. A group of 18 panelists participated in the magnitude estimation sessions and this had decreased to the final 12 panelists who also completed the labelled magnitude scale studies.

3.2.2.2.2 Assessor Selection using “Sequential Testing”

Assessor selection was designed to identify panelists with the olfactory sensitivity to perform the required sensory tasks and the personal qualities to participate in the test, including availability, interest, and attitude. Sequential testing utilized difference tests that are administered with preset statistical criteria for assessor selection. It allowed the decision of “accept for panel”, “reject for panel” or “continue testing” to be made through the use of a pre-set control graph of the statistical criteria (Figure 3.1). Several researchers have described these tests as being meant to “economize” on the number of tests which must be conducted in order to accept or reject a panel trainee while providing a statistical basis on which to base this decision (Meilgaard et al., 1999; Munoz et al., 1992; Amerine et. al., 1965). This method was based on the *a priori* selection of the statistical levels of α & β probabilities for the level of performance of the assessors and the use of difference tests such as triangle, duo-trio, and paired comparison-difference. These methods have been applied in taint analysis of aquatic systems (Environment Canada, 1997).

Sequential testing requires the calculation of control graphs to evaluate the performance of each of the assessors. The criteria used in calculating the control graph were based on the type of test and the levels of statistical significance. The recommended levels of statistical significance were $\alpha=0.05$, $\beta=0.05$. The values of p_0 and p_1 were based on the probability of correctly guessing the odd sample for the triangle test with $p_0 = 1$ in 3 chance of guessing correctly and $p_1 = 2$ in 3 chance of guessing incorrectly. The graph used for this work is given in Figure 3.1 and was calculated using the method given in both Meilgaard et al. (1999) and Amerine et. al. (1965).

The test utilized sets of 6 triangle tests as shown in Table 3.2. The panelist continued testing at Level 1 until a decision could be made to “accept” or “reject” based on the number of correct identifications of the odd sample. On a subsequent test day, the candidate panelist was given a set of 6 triangle tests at Level 2, and continued testing until the final decision to “accept” or “reject” could be made. All of the candidate panelists were able to correctly identify sufficient samples by 12 sets of triangle tests to allow them to continue to the data collection phase of the work. The triangle test used was the 3-alternative forced choice form of the test for all sessions, with the odd sample being the strongest sample, i.e., either 40 ppm or 80 ppm 1-butanol in the set.

Samples were presented for evaluation using standard wide-mouth 500-ml Erlenmeyer flasks that contained 200 ml of the appropriate solution. Flasks were lidded with formed aluminum foil caps (new each time - never reused). Fresh samples were prepared daily. Samples, coded with 3-digit random number codes, were presented in appropriate sets to the panelists. Odor samples were used only for a two-hour period, then replaced. In the evaluation procedure the panelist gently swirled the flask to equilibrate the headspace concentration of 1-butanol, then raised the cap, sniffed the sample and replaced the cap to allow the headspace volatiles to regenerate. A flask of distilled water was provided for rinsing by sniffing between samples.

Table 3.2 Triangle test samples used for selection panels.		
Level 1 of screening, test series is randomized set of		
3 sets of	2 flasks water, 1 flask of 40 ppm 1-butanol	presented in random sequence
3 sets of	2 flasks water, 1 flask of 80 ppm 1-butanol	
Level 2 of screening, test series is randomized set of		
3 sets of	2 flasks of 20 ppm 1-butanol, 1 flask of 80 ppm 1-butanol	presented in random sequence
3 sets of	2 flasks of 10 ppm 1-butanol, 1 flask of 40 ppm 1-butanol	

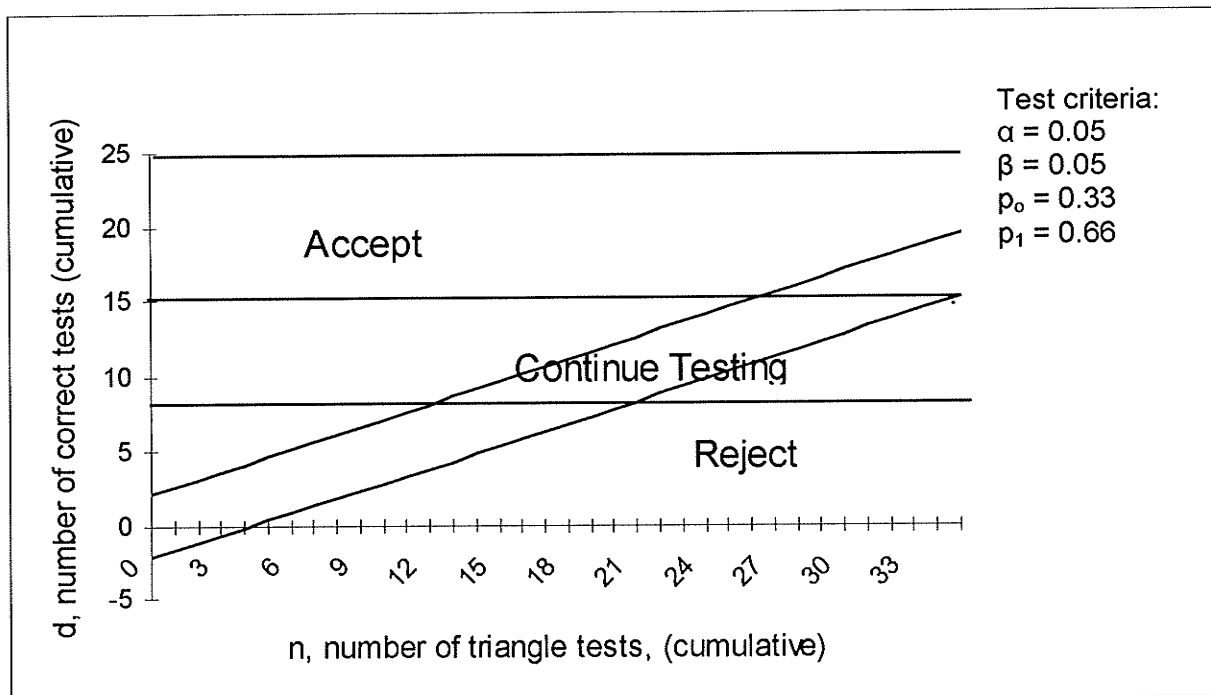


Figure 3.1 Sequential analysis graph for triangle tests used for selection of panelists.

3.2.2.2.3 Panel Training:

Panelists were trained to familiarize themselves with the format and the use of each of the scales and with the stimulus. Three sessions were held to allow panelists to gain experience with each of the scales prior to beginning the study. A “refresher” session was held before the beginning of the labelled magnitude scale sessions. The commonly used method of “lengths of lines” and “areas of figures” was used to demonstrate both magnitude estimation and the labelled magnitude scale procedures. These are shown in Appendix C and consisted of paper and pencil exercises and a discussion session for the results. This was followed by concentrations of the 1-butanol to give them experience with the actual stimulus prior to testing. There was no attempt to standardize the values assigned to the samples, although comparisons were allowed during the session to give the panelists confidence in their abilities through the relative ranking of the samples (i.e., correct identification of increasing concentrations). Samples were not standardized

to “scale values” as this was accommodated in the data analysis through data normalization, which was used to bring the differing lengths of scales to a common mean.

3.2.2.2.4 Sensory Analysis – Data Collection

The study design included three replications for each of the scaling methods and each of the 12 concentrations used. The sequence of testing was to first conduct the magnitude estimation study completely using all of the 18 selected assessors. The next sequence of testing was the labelled magnitude scale. This second data set was collected approximately 3 weeks after the first series to attempt to reduce the carryover effect. There was some attrition in the panel during this time, and only 12 of the panelists were available for the labelled magnitude scale portion of the study.

The ballots and instructions for magnitude estimation and the labelled magnitude scale are shown in Appendices D and E. The reference sample for magnitude estimation, which was given a value of 10, was 250 ppm 1-butanol. The concentration of the warm-up sample for the labelled magnitude scale was 250 ppm 1-butanol. Samples were presented for evaluation using standard wide-mouth 500-ml Erlenmeyer flasks that contained 200 ml of the appropriate solution. Flasks were lidded with formed aluminum foil caps (new each time - never reused). Fresh samples were prepared daily. Samples, coded with 3-digit random number codes, were presented in random order sets to the panelists. Odor samples were used only for a two-hour period, then replaced. In the evaluation procedure the panelist gently swirled the flask to equilibrate the headspace concentration of 1-butanol, then raised the cap, sniffed the sample and replaced the cap to allow the headspace volatiles to regenerate. A flask of distilled water was provided for rinsing by sniffing between samples.

3.2.2.3 Data Analysis of Experiment 1

In order to be able to proceed with log-transformations of the data, any sample that had been assigned a value of 0 was recorded as 0.01. The aim of the analysis was the calculation of the power law exponents for each of the tests and the comparison of these exponents. This was done by first converting the data to logarithms and then normalizing the log-transformed data. This was followed by the calculation of the linear regression of the sensory scores (Y) and the stimulus concentrations (X) and the comparison of the lines for equal slopes.

The data was prepared for analysis by normalization using the method of modulus equalization (Moskowitz & Jacobs, 1988). The purpose of this was to bring all of the individual scales to a common length by having the geometric mean of each panelist equal to the geometric mean of every other panelist. An essential requirement for this method was that all of the panelists must each evaluate the same stimuli. This was accomplished by first calculating the geometric mean of each panelists's sensory scores (GM_i) and the geometric mean of the panel (GM_o). The difference between the geometric mean of each panelists's ratings and the geometric mean of the panel ($DGM_i = GM_i - GM_o$) was calculated. Finally, the DGM_i was subtracted from (or added to) each panelist's ratings so that the geometric mean of each panelist's ratings became equal to the geometric mean of the panel. (Moskowitz & Jacobs, 1988).

The data were calculated for only the 12 assessors who participated in both of the panel series. The regression lines were calculated and compared using SAS Version 8 (SAS Institute, Inc., Cary, NC) using the SYSLIN procedure with "seemingly unrelated regression" (SUR). This method was chosen as the data had been collected using the same individuals as panel members for each of the methods (magnitude estimation and the labelled magnitude scale). Because of this, the errors in the different equations were considered to be correlated and the efficiency of the estimation could be improved by taking these cross-equation correlations into account. (SAS, 2002). The regression lines for each of the data sets were calculated and the results of the slope and intercept shown in Table 3.3. The slope of the regression line corresponded to the exponent

of the Power Law when calculated on log transformed data. The intercept was equal to the constant for the Power Law formula ($\log S = \log k + n \log I$, see Section 2.1.3).

Table 3.3. Mean sensory scores for ratio data from magnitude estimation and the labelled magnitude scale. ^a		
1-Butanol concentration in water (ppm)	Panel means for magnitude estimation ^b	Panel means for the labelled magnitude scale ^b
5	-1.178	-1.080
10	-1.152	-0.896
25	-0.586	-0.346
50	-0.432	-0.300
100	-0.176	-0.101
250 ^c	0.01	0.042
500	0.277	0.180
1000	0.354	0.262
2500	0.523	0.457
5000	0.684	0.521
10000	0.809	0.577
20000	0.879	0.678
n (= exponent for the Power Law)	0.592	0.463
k (= constant for the Power Law)	-1.4930	-1.1714
R ²	0.9688	0.9422
F (1, 865) for comparisons of the two slopes	18.65 (significant at P < 0.0001)	
^a as normalized log values for each concentration tested		
^b mean of all values over 3 replications using normalized magnitude estimation or labelled magnitude scale data.		
^c Warm-up sample for the labelled magnitude scale and reference standard for magnitude estimation.		
Note: values of 0 are not allowed. If assigned by a panelist, the data point was converted to 0.01.		

3.2.3 Results and Discussion of Experiment 1

The values calculated for Stevens' power law (through linear regression) for ME and LMS relating the physical and sensory intensities of the stimuli are shown in Table 3.3 and the regression lines are illustrated in Figure 3.2. When the two lines were compared through the

SYSLIN procedure with “seemingly unrelated regression” (SUR), the calculated $F = 18.65$ ($df = 1, 860$), which was significant at $p < 0.0001$. This indicated that in this test, the calculated exponents for Stevens’ power law were not the same and that the exponent for the labelled magnitude scale data was significantly smaller than that for the magnitude estimation data. In applications, the calculations using labelled magnitude scale values would overestimate the response at the lower concentrations and underestimate the response at the higher concentrations.

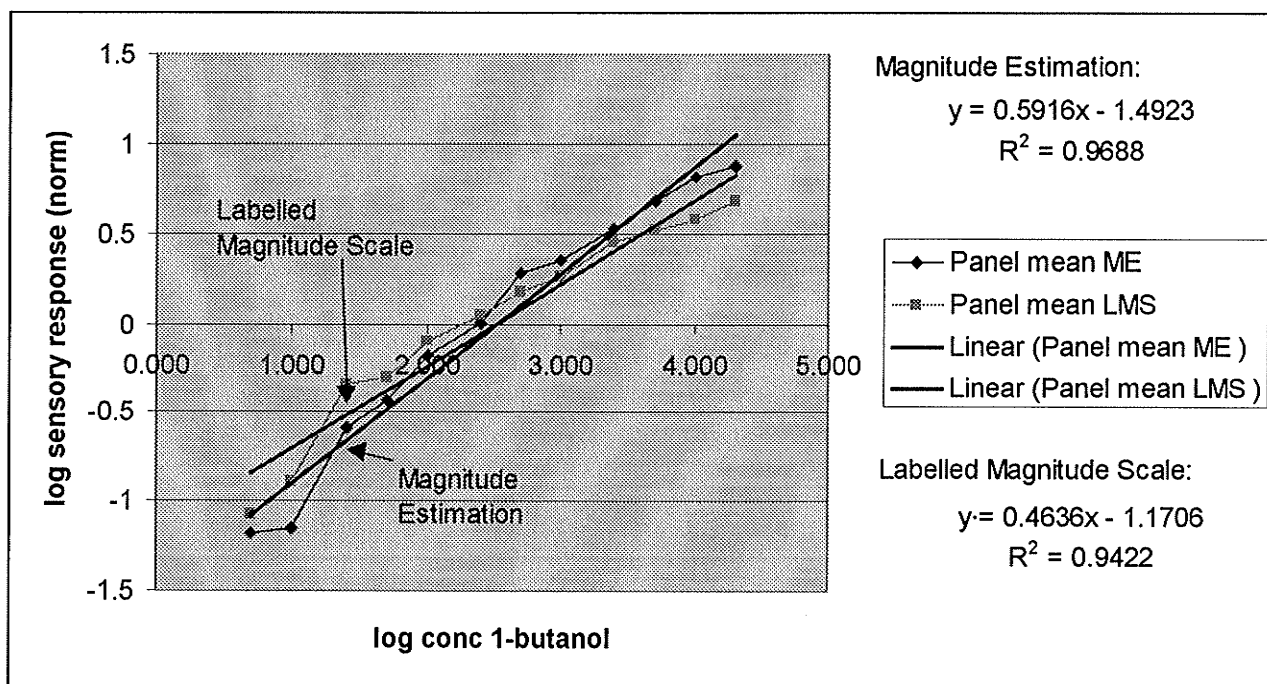


Figure 3.2. Results of linear regression analysis for each of the scaling methods. Each is shown both as points and as the calculated line. All values are in logarithms for each of the axes.

The first hypothesis was rejected because the values for n for the two scaling methods are significantly different. However, they were not different from the range of exponents for 1-butanol or from the overall exponent calculated from the references used in the review paper by Patte et al., (1975). These researchers (i.e., Patte et al., 1975) reported values from the literature for the exponent for 1-butanol using varying test conditions. Previously reported values varied from 0.22 to 1.00. However, a value of 0.52 was the standardized slope to characterize 1-

butanol. This value compared favorably to the exponents for magnitude estimation (0.59) the labelled magnitude scale (0.46) obtained here. The average of the two slopes found here was 0.525, essentially the same as the reported value for the standardized slope. Moskowitz et al. (1974) found that the exponent for a 1-butanol scale using dynamic dilution olfactometry and presenting the stimulus in air was 0.66 (using 250 ppm in air as the reference standard), so once again, the values found here were within the general range in the literature.

The reason for the differences in the exponents found here were somewhat speculative. The first obvious consideration was that there was a real difference in the two values, which was not necessarily validated here since both of the components fall within the range of the literature values for magnitude estimation. Another was that these differences were due to differences in the panels and the level of training, from the first to the second series from a learning effect. This was a newly trained panel (especially at first), representative of the type often used in work done at universities, and unfamiliar with the stimulus used. The panels were conducted sequentially with all of the data for magnitude estimation data collected first and then, after a three-week hiatus, all of the data for the labelled magnitude scale. This was done in order to avoid confusion for the panelists' in the scaling methods and the rest period between experiments was introduced to attempt to reduce any order effect. There could have been a training effect on the second series of panels from the experience with the stimulus during the first series of panels.

3.3 Experiment 2. Electronic Nose Analyses of 1-Butanol Solutions

3.3.1. Introduction to Experiment 2

An expert system, to be useful as a predictor, must provide the information that is as reliable as the methodology it replaces. In this case, the electronic nose must provide readings that correlate highly with those of the sensory panel. The 1-butanol data provided an ideal test series to examine this relationship in that the samples were completely controlled and repeatable over an extended series of time. While the samples were tested over a long time with the sensory

data collected in 1999 and the electronic nose data generated in February 2004, the samples were prepared in the same way from the same test materials and provide a reliable comparison.

The objectives for this portion of the study were to establish electronic nose test conditions appropriate to these samples and to test the series of 1-butanol solutions. This would allow the examination of the relationships between the concentration of 1-butanol of the samples, the sensory scores, and the electronic nose sensor responses.

3.3.2 Methods and Materials

3.3.2.1 Electronic Nose Analysis

Tests were conducted using an Alpha MOS Fox 3000 Electronic Nose equipped with 12 metal oxide sensors. Prepared samples were placed into a sampling tray for the auto-sampler and held at room temperature (20-22°C) during the sampling process. Samples were transferred sequentially to the incubator/heating block and gently agitated at constant rpm/directional cycle (500 rpm) to facilitate headspace sample production. The headspace sample was drawn into the syringe and transferred to the injection port of the electronic nose. Sensor response data were collected for 120 s followed by a 1080-sec delay before injection of the next sample. The carrier gas flow rate maintained at 150 ml per min is oxygen/nitrogen at 20% O₂ ± 1% (i.e., 19.8 to 20.2 % O₂) and with impurities specified as H₂O < 5ppm, C_nH_m < 5ppm, O₂ + N₂ > 99.95%, O₂ = 20% +/- 1%.

The specific test conditions used for analysis of the 1-butanol samples were an incubation temperature of 50°C, an incubation time of 5 minutes (using standard agitation conditions of 500 rpm), sample size of 1 ml per 10 ml vial, with 4 replications of each sample, injection sample volume of 500 µl headspace volatiles drawn as the sample, and 150 ml/min air flow of carrier gas within the unit. Table 3.4 shows the concentrations of 1-butanol tested and the coding used for the samples in the electronic nose analyses.

Table 3.4 Concentrations of 1-butanol used based on ASTM E-544-99 and codes used in electronic nose analyses.	
Concentration in water ppm	Code for Electronic Nose Maps and Graphs
5 ^a	L01
10	L02
25	L03
50	L04
100	L05
250	L06
500	L07
1000	L08
2500	L09
5000	L10
10000	L11
20000	L12
^a this concentration is below the recommended starting point of 10 ppm in water and should be below threshold.	

3.3.2.2 Data Analysis

The numerical values of the changes in sensor resistance were recorded as individual response patterns for each of the 12 metal oxide sensors by the computer system operated through the Alpha MOS AlphaSoft V8.0 software. These values were transformed into a “library” file, which contained all the sensor patterns to be used in the analyses for each of the sample series. The analyses performed were from the multivariate statistical analyses contained in the program including principal component analysis (PCA) and linear regression using the “Sensory Score Correlation” (SSC) analysis. PCA allowed the evaluation of the ability of the electronic nose to detect differences within and among sample groups and provides an assessment of how well the instrument was able to differentiate samples. The differentiation was shown by the value of the Discrimination Index (DI), which was given as a percentage varying from –100% to +100%. Only discrimination index values above 80% were considered to be “good” results in terms of the differentiation among samples. The Sensory Score Correlation (SSC) subroutine allowed correlation using linear relationships and this was chosen as the sensory means were in their

normalized log-transformed format and so could be used in a linear relationship. A correlation coefficient greater than 0.8 was considered acceptable.

3.3.3. Results and Discussion

The ability of the electronic nose to distinguish among the concentrations of 1-butanol are demonstrated in the PCA maps in Figures 3.3 and 3.4. The codes for the concentrations are given in Table 3.1 and were designed to simplify the data coding with the electronic nose. In Figure 3.3, all of the concentrations including 5 ppm were included in the analysis, and there was an overlap between 5 ppm and 10 ppm, which caused the Discrimination Index to be low and to indicate low discrimination. Visual examination of the map showed that this is the only overlap and that all of the other samples were clearly discriminated. As was noted in the section on sensory analysis, 5 ppm 1-butanol was generally not included in scales designed for human use as the concentration was below threshold. It would seem that this might be the case as well for this electronic nose system. ASTM E544-99 described concentrations of 1-butanol below 10 ppm as being too weak to be perceived by human panels.

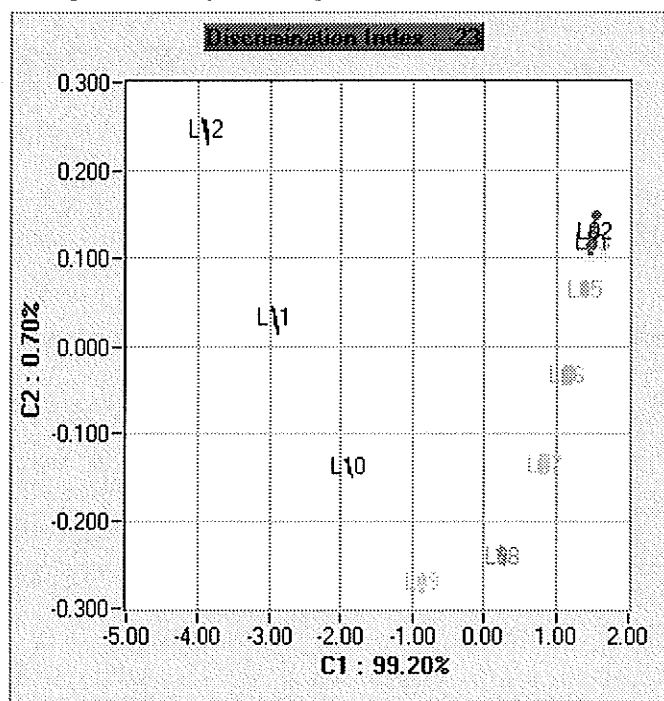


Figure 3.3 Principal components analysis (PCA) map of all 12 concentrations of 1-butanol (using 4 reps of each concentration). The low discrimination index is caused by the overlapping of the lowest concentration of 1-butanol (L01= 5 ppm) with the next concentration (L02 = 10 ppm).

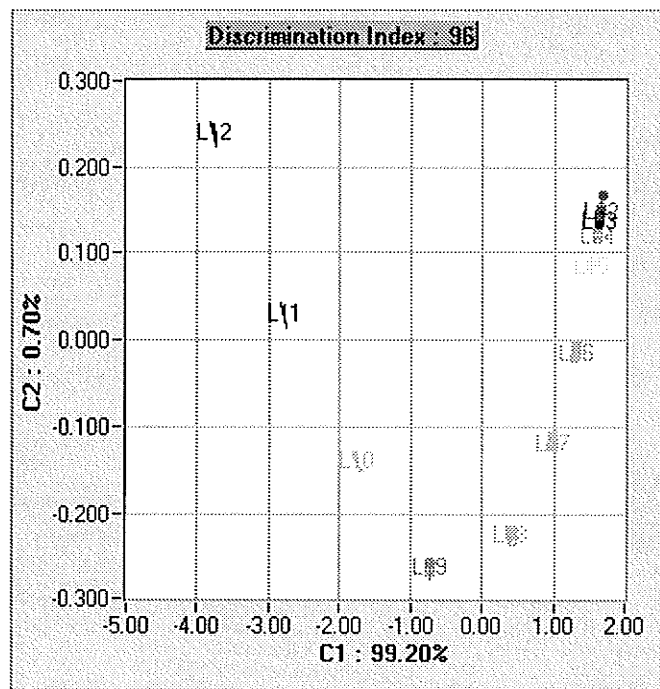


Figure 3.4 PCA map of the concentrations of 1-butanol with the L01 (5 ppm) sample removed. The discrimination index is now 96% (maximum = 100%) showing the excellent separation of the samples. The lowest concentration used here is the lowest one given as useful by ASTM E544-99, i.e. 10 ppm.

The discrimination index (DI) was improved by removing L01 (5 ppm) from the analysis. At this point the discrimination index was now 96% and the electronic nose was easily able to discriminate among the concentrations that were most important in this and future testing. Therefore Hypothesis II was accepted.

This discrimination was further examined relative to the sensory assessments of the intensity of the 1-butanol concentrations using the data from both scaling methods. This was done through the "sensory score correlation" analysis in AlphaSoft version 8.0, and the results were shown in Figures 3.5 a and b for the magnitude estimation data and Figures 3.6 a and b for the labelled magnitude scale data and the correlation coefficients shown in Table 3.5. It was clear that the sensory and the electronic nose data correlated very well for both of the scaling methods and that either could be used as a data source for relating to the electronic nose data, and Hypothesis III was accepted.

Table 3.5 Correlation coefficients (R) calculated through linear regression (SSC) for the sensory data and the electronic nose response patterns.		
Scale used for data collection	Correlation coefficient with all 12 samples included	Correlation coefficient with all L01 samples (5ppm) removed
Magnitude Estimation	0.97	0.98
Labelled Magnitude Scale	0.95	0.97

3.4 Discussion and Conclusions

The values for the exponents for 1-butanol in this study were found to be statistically different. The exponent using magnitude estimation was 0.59 while that found using the labelled magnitude scale was 0.46. However, both were within the range of values found in the sensory literature.

The electronic nose could differentiate the samples easily when the one sample that is below human threshold perception was eliminated. The electronic nose correlated very well with both of the scaling methods. Because one method could not be eliminated by performance, the decision on which one to use with was based on the panelists' ease of response to the data collection, the labelled magnitude scale.

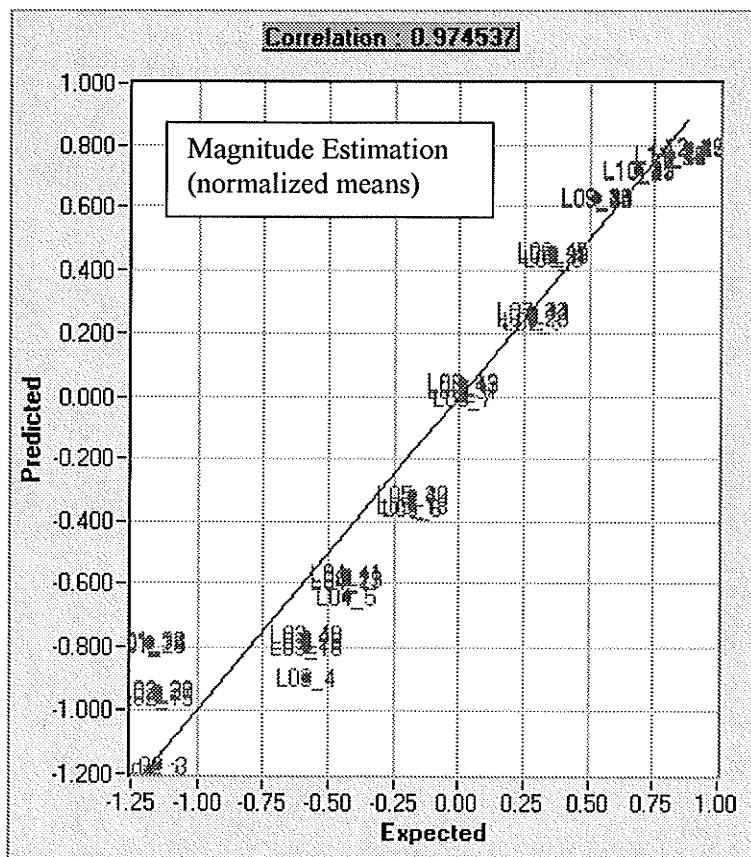


Figure 3.5 (a) Sensory Score Correlation (SSC) using magnitude estimation means (from normalized data and as logs) for all 12 of the concentrations tested. $R = 0.97$ for these data.

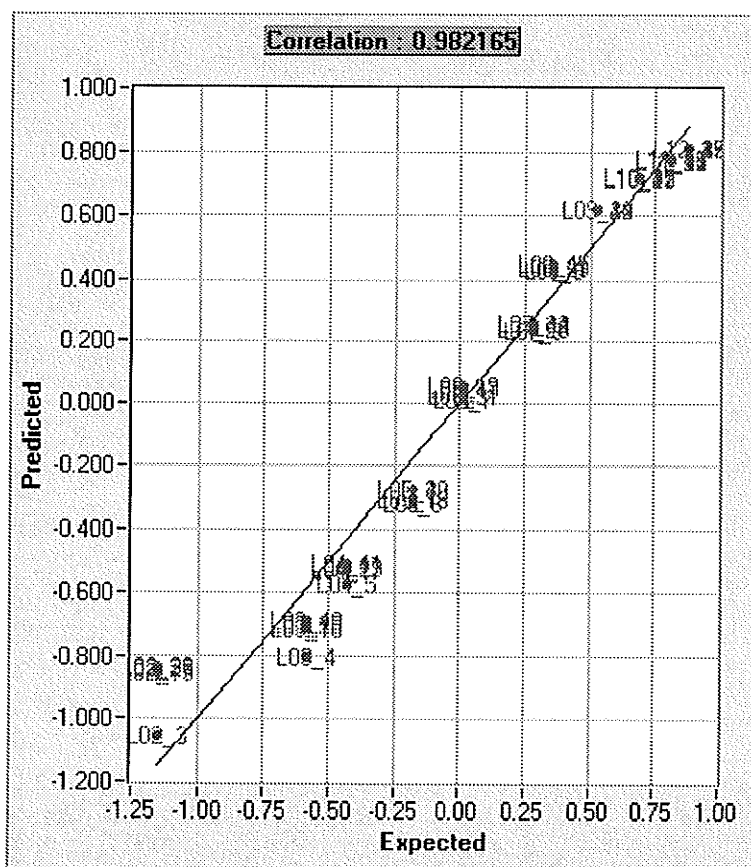


Figure 3.5 (b) Sensory Score Correlation (SSC) using magnitude estimation means (from normalized data and as logs) with the lowest (subthreshold) concentration removed. $R = 0.98$ for these data.

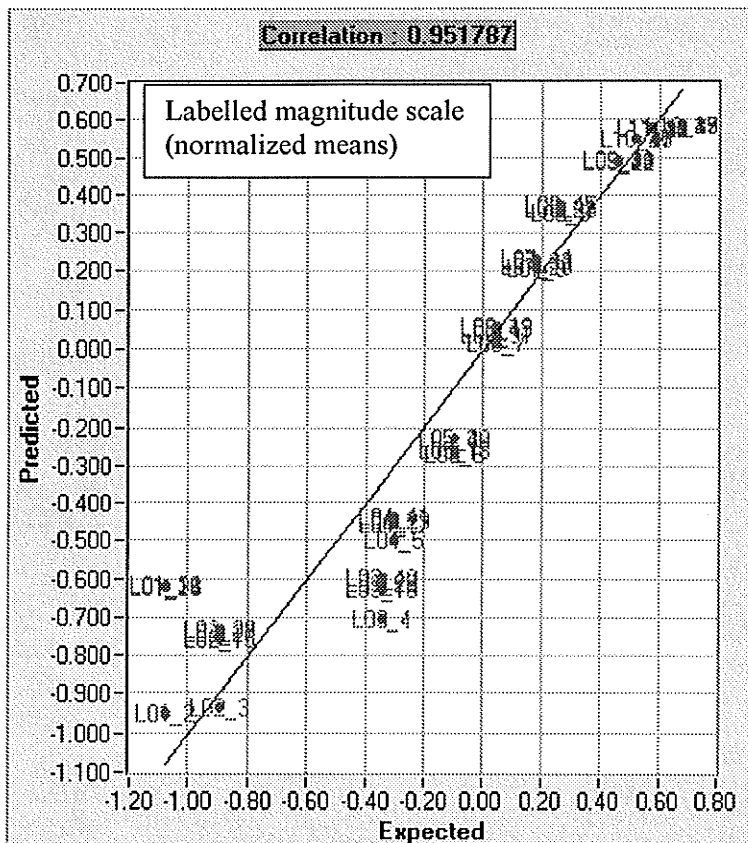


Figure 3.6 (a) Sensory Score Correlation (SSC) using labelled magnitude scale means (from normalized data and as logs) for all 12 of the concentrations tested. $R = 0.95$ for these data.

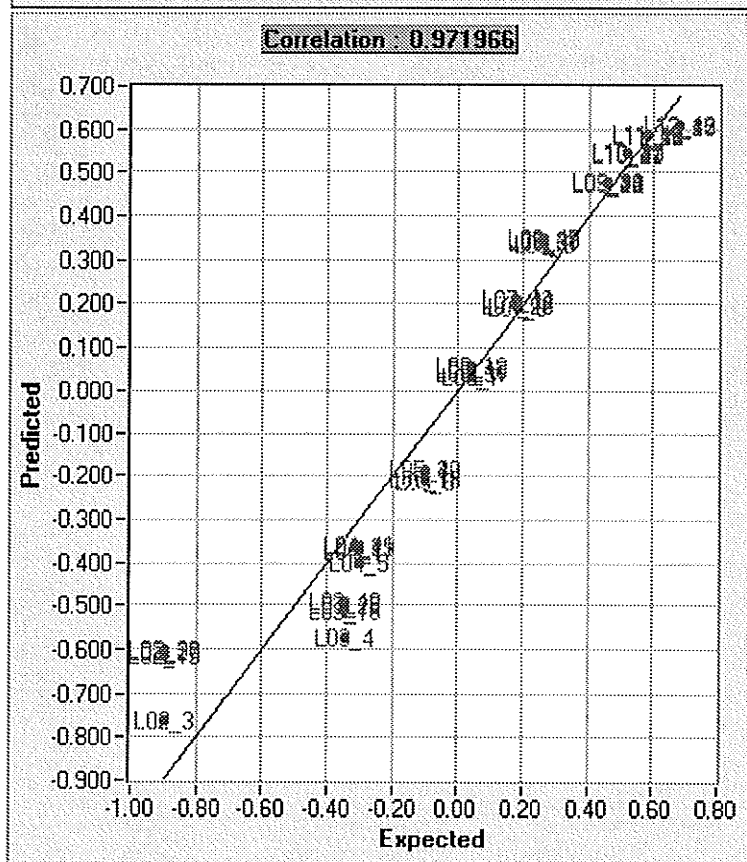


Figure 3.6 (b) Sensory Score Correlation (SSC) using labelled magnitude scale means (from normalized data and as logs) with the lowest (subthreshold) concentration removed. $R = 0.97$ for these data.

Chapter 4

Study #2: Evaluation of Cloth Sources for Uptake of Malodors in Environmental Testing

4.1 Introduction

Sampling environmental malodor by stabilizing it on cloth has interested workers over a number of years. Some studies have attempted to standardize this work for larger scale applications. One consideration, which had not been tested beyond simple trials, was the effect of the type of cloth selected on the success of the sampling method. If cloth sampling was to be useful, it needed to be based on knowledge of the sampling materials themselves. Most studies to date have used cotton flannel of unnamed sources and physical properties for odor collection, and one early study included wool flannel. If these methods were to be useful, they must perform at least as well as current methods and be able to be related mathematically to those results.

The current sampling methods used a combination of sensory testing methods, in the field and in the laboratory. The field studies involved sending individuals into the areas where the malodors occur and having them measure odor present in the environment (see Chapter 6). The laboratory studies involved taking large Tedlar®-bag samples of air back to the laboratory for analysis with a dynamic dilution olfactometer. These were generally well accepted and provide objective data when used with selected, trained assessors. The data produced with a dynamic dilution olfactometer is limited to the degree of dilution associated with perception, a measure of threshold for the odorant or mixture tested. This provided a relative measure of intensity, but not a direct measure. Disadvantages of the method included the size of the samples required and the expense associated with the disposable sampling bags. A standard method of measuring the odor intensity would be a useful tool to provide numerical measurements of odor intensity. The addition of standards to this system allowed calibration of the measurements and comparisons both within and across tests.

Observations on the uptake of odors on cloth swatches have been reported since the 1980s and arose initially from the observations of workers that clothing worn while in the barns

retained the odors for some period of time. This stabilization of the odors began to be explored to a limited degree as a pathway to transport the odors to another location for sensory analysis. Several authors have used exposure of cloth swatches to stabilize odors for transport to a laboratory for further analysis (Miner & Licht, 1981; Williams & Schiffman, 1995; Nicolai et al., 1997; Labance et al., 1999). Various types of standardization and presentation have been reported including placing of swatches of specified sizes within barns and at air outlets for controlled amounts of time. However, the exposure was relatively unregulated and depended on the conditions present in the environment and any other variables introduced through this pathway that were not accounted for in the testing. After exposure the swatches have been placed into containers such as glass jars, Tedlar® bags and plastic bags to stabilize them for presentation to sensory panelists for responses to measure the strength of the odor. The cloth used has generally been cotton flannel, while one study used wool flannel. The fabric sources and condition have not generally been specified. The size of swatch is generally given, but not the source of the material and the degree of pretreatment given the samples. The assumption must be made that the fabric was obtained from fabric shops and was likely treated with dyes and other standard finishes. Washing the fabric was cited as a preparation method in some references.

Initial work on the controlled exposure of cloth swatches (cotton flannel) to manure malodors has been reported by Zhang et al., (1999). This work presented the evaluation of cloth swatches that had been exposed to specified volumes of air for specific time periods and showed the successful objective sensory measurement of the uptake of the odorant onto the fabrics. This work on a standardized swatch test was designed to provide simpler sampling procedures, which are less cumbersome and expensive. It could provide greater test flexibility in the format of the sensory analysis methodology that can be used and allow the comparison of results within and across testing times.

Electronic nose technology has been successfully used for the characterization of environmental malodors from a variety of industrial and agricultural sources (Persaud et al.,

1996; Classen, et al., 1997; Maricou et al., 1998; Romain et al., 2000; Nicolas et al., 2000). In all cases the sampling was done using gaseous samples taken from Tedlar®, or similar, sampling bags. The flexibility of the sampling system being proposed makes it possible to test the cloth swatches through electronic nose analysis in the same manner in which samples are presented for sensory analysis.

The specific objectives for this study were to develop the components for a method of standardized odor sampling of air-borne malodors using cloth swatches and to test the odor levels through analytical sensory analysis and the application of electronic nose technology. The hypothesis was that different fabrics would adsorb odors to different degrees. A second hypothesis was that odor adsorption will be associated with measurable chemical and physical attributes of the fabrics. The fabric that has been most often reported in previous studies, cotton flannel, would be used so that all other fabrics would be analyzed relative to that fabric. The fabrics were from a standard test fabric supplier, so that finishes and dyes would not be present. The method included stabilizing swine odor on selected cloth swatches by exposure to controlled amounts of odorous air so that the odor could be removed from the sampling area and taken to a sensory facility for evaluation. Two of the issues in fabric selection were the ability to adsorb and retain odor – its substantivity – and any intrinsic odor of the fibre/fabric that may be present.

4.1.1 Objectives and Hypotheses

The overall objective of this study was to systematically evaluate a selection of fabrics for the ability to adsorb a malodor, retain it, and subsequently release it for sensory and electronic nose evaluation. The selection criteria for the fabrics included different fibres, different structures, no dyes or production finishing and that, initially, approximately similar fabric weights. The evaluations used were sensory analysis in the form of a ratio scale (the labelled magnitude scale) and a linear scale (difference-from-control) and electronic nose analysis using an Alpha MOS Fox 3000 electronic nose. A secondary objective was to evaluate the substantivity of the samples for repeated use during sensory testing.

an Alpha MOS Fox 3000 electronic nose. A secondary objective was to evaluate the substantivity of the samples for repeated use during sensory testing.

The hypothesis being tested using sensory analysis were:

Hypothesis I: that all cloth types would adsorb the volatile components associated with swine malodors to some degree that is measurable using sensory analysis using the labelled magnitude scale (ratio data).

Hypothesis II: that all cloth types would adsorb the volatile components associated with swine malodors to some degree that is measurable using sensory analysis using the difference-from-control test (linear data).

Hypothesis III: that not all types of cloth would adsorb odors to the same level of perceived sensory intensity as measured by the labelled magnitude scale (ratio data) and can be compared through analysis of variance and post hoc comparisons.

Hypothesis IV: that not all types of cloth would adsorb odors to the same level of perceived sensory intensity as measured by the difference-from-control test (linear data) and can be compared through analysis of variance and *post hoc* comparisons.

Hypothesis V: that the physical properties of the fabrics would affect the degree to which odor was adsorbed by the fabrics as measured by the labelled magnitude scale (ratio data).

Hypothesis VI: that the physical properties of the fabrics would affect the degree to which odor was adsorbed by the fabrics as measured by the difference-from-control test (linear data).

The hypotheses being tested using the electronic nose are:

Hypothesis VII: that the electronic nose was able to detect the difference between samples of each cloth, unexposed and exposed to swine odor, when compared through principal component analysis.

Hypothesis VIII: that not all types of cloth would adsorb odors to the same level as measured by the electronic nose as compared through principal component analysis.

Hypothesis IX: that the physical properties of the fabrics would affect the degree to which odor was adsorbed by the fabrics as measured by the electronic nose as measured by linear regression analysis.

4.2 Methods and Materials:

The study compared 13 fabrics exposed to a model system of odorants representing compounds found in the odor of hog manure in order to evaluate the suitability of different fabric sources for the uptake of odors for laboratory analysis.

The components of the experimental design included 13 different fabrics, varying by fibre source (chemical characteristics) and weave structure, (physical characteristics) were selected for testing. Samples of unexposed fabric were compared to exposed samples. These were prepared using an odor exposure system that could be applied in both laboratory test conditions was developed from an existing system. This allowed fine control over the amount of odorant to which the fabric swatches were exposed. A standard odor source was used for controlled exposure of fabrics, a swine odor simulant compounded from a mixture of chemicals identified as important in the production of this odor. Sensory panel work included panel screening using the 1-butanol triangle tests designed for selection of assessors, who were able to distinguish between concentrations of a standard odorant. This was followed by data collection using two types of scaling methods, one linear (difference-from-control) and one ratio (labelled magnitude scale with normalized data). Data was also collected using electronic nose analysis of all of the fabric samples in both the unexposed and exposed state for comparison to the sensory data.

4.2.1 Overall Experimental Design

In the study, 13 fabrics were tested as unexposed and exposed swatches through three replications for each of the sensory and electronic nose analyses. Four sets of samples were prepared for each of the panel sessions, and each was used up to four times. The position of

evaluation of each of the cassettes was recorded along with the assigned scale value for each assessor and used to evaluate the stability of the samples over the test session. Thirteen assessors were selected to participate in the panel sessions. Ten completed all of the difference-from-control panel sessions and 11 completed all of the labelled magnitude scale sessions. The data for this completely balanced design was analyzed within each of the types of scales using SAS Version 8 (SAS Institute, 1999-2001) and SPSS Version 10 (SPSS, Inc., 1999).

All of the exposures and sensory panel and electronic nose studies were conducted in the CFIA Sensory Science Laboratory at the Freshwater Institute in Winnipeg, MB. Textile tests – with the exception of yarn counts – were conducted at the Textile Testing Service, Department of Clothing and Textiles, University of Manitoba.

4.2.2 The Exposure System

The exposure system in this study was a modification of the one used by Zhang et al. (1999). The system is shown in Figure 4.1 and consisted of a 500-ml. vacuum flask, which contained the odor source (here the swine odor simulant), a three-piece air sampling cassette, which contained the prepared swatch, and a pump, which could be calibrated to control the rate at which air from the odor source was drawn through the cloth swatch. The principle of the system was that odorized air was drawn through the fabric by use of a pump calibrated to specific flow rates. The odorized air was in contact only with the glass of the flask, the plastic of the cassette and the cloth contained within the cassette. Contact with any tubing occurred only after the cloth exposure and did not affect the generated air or the prepared swatch.

For this work, 200 ml of the swine odor simulant was placed in the flask, and the exposure rate for the swatches was standardized at 5 litres per minute for 2 min. The cassette was sealed immediately after exposure and presented to sensory panelists within 6 h. Swatches for electronic nose analysis were immediately placed into 10-ml sampling vials and the Teflon®

lined metal lids sealed air tight with a crimping tool. Fabric swatches were oriented in the vials for exposure of the maximally exposed fabric surface to the inside of the container.

In their earlier study, Zhang et al. (1999) observed that the odor intensity on the cloth swatches decreased with each successive opening of the cassette. These changes in odor intensity were associated as well with the humidity of the air to which the cotton flannel has been exposed. This effect would likely vary with the hygroscopicity of the fabric. In the current work, the exposure of the swatch to the outside air and the resulting dissipation of the sample were controlled through a different sample testing condition. The three-piece cassettes used to contain the cloth swatches had top and bottom ports that are closed with color-coded plugs. Preliminary testing evaluated the effectiveness of controlled opening of the cassettes for sample evaluations. Instead of the cassettes being opened completely as in previous work, only the plugs were removed and the cassette placed near the panelist's nostril. Sniffs of air were drawn through the fabric, but the fabric was only exposed to the amount of air drawn through the cassette by the assessor. Plugs were replaced immediately. Cassettes were used up to 4 times for evaluation and the time condition recorded for each assessor.

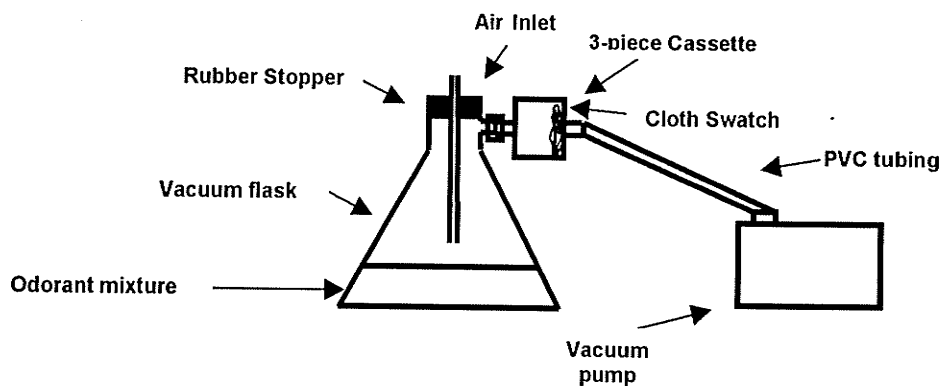


Figure 4.1 Modified exposure system used to treat the cloth swatches with the swine odor simulant.

4.2.3 Simulated Swine Odor Mixture

A standard odor mixture was prepared based on the formulation taken from Persaud et al. (1996). The mixture was modified slightly to facilitate ongoing preparation of the sample for use. Limited qualitative testing indicated that the mixture was an effective swine odor simulant and was used without further modification. The original and modified formulas are shown in Table 4.1.

Table 4.1. Composition of swine odor simulant.			
Sample Component #	Component	Mixture used by Persaud et al. (1996) ppm	Swine Odor Simulant ppm
1	acetic acid	1365	1500
2	propanoic acid (propionic acid)	358	375
3	2-methyl propanoic acid (isobutyric acid)	604	600
4	butanoic acid (n-butyric acid)	237	250
5	3-methyl butanoic acid (isovaleric acid)	301	300
6	pentanoic acid (N-valeric acid)	90	100
7	phenol	21	25
8	4-methyl phenol (p-cresol)	62	75
9	indole	6.6	7.5
10	3-methyl indole (skatole)	3.7	5
11	ammonium hydroxide (NH ₄ OH) 5% stock solution	adjust to pH 8.2	adjust to pH 8.2

4.2.4 Selection and Characterization of Fabrics for the Cloth Swatches

The fabrics selected for testing are shown in Table 2. All fabrics except activated carbon cloth were obtained as yardage from TestFabrics, West Pittston, PA. The activated carbon cloth was obtained from Calgon Carbon Corporation (Pittsburgh, PA). The fabrics selected represent different fibre sources: natural fibres were cellulose (cotton, linen and rayon), protein (wool, silk), and synthetic (rayon, Dacron (nylon), polypropylene, and activated carbon cloth). There were different surface characteristics, weave structures, and surface topographies including smooth, brushed, and pile fabrics.

The circular swatches were cut from yardage using a mechanical system consisting of a drill press fitted with a custom 37-mm diameter cutter. The swatch size was dictated by the size of the air-sampling cassette. The swatches were pretreated for removal of any extraneous odors by heating for 1 h at 85°C in a drying oven dedicated for this purpose. The treated swatches were placed in sterilized glass jars with aluminum foil-lined lids and sealed for storage until used. The only contact surfaces were glass, metal and aluminum foil. Swatches were handled with clean forceps for placement into cassettes and sampling vials.

Table 4.2. Fabrics selected for evaluation for odor uptake.

Code used in the study	Catalogue Number	Sample Code (electronic nose)	Fabric Description
1	425	COT	cotton - flannel, bleached
2	419	CTB	cotton broadcloth, bleached, mercerized, combed
3	437W	CTK	cotton - knit - bleached cotton T-shirt fabric
4	420BR	CTT	cotton - 9.5 oz, bleached terry cloth
5	494	CTW	cotton - twill, bleached, mercerized
6	523	WOL	wool - worsted flannel
7	530	WLC	wool challis
8	609	SLK	silk habutae 8 mm
9	L54	LIN	linen - suiting
10	266	RAY	spun viscose challis (rayon)
11	777	DAC	Dacron type 54 (disperse dyeable)
12	983	PLY	spun polypropylene
13**	n/a	ACC	activated carbon cloth
* Fabric source for samples 1 to 12: TestFabrics, Inc., P.O. Box 26, West Pittston, PA, USA, 18643			
** Fabric source for sample 13: Calgon Carbon Corporation, Calgon Carbon Drive, Pittsburgh, PA 15201			

Fabrics were characterized for their physical properties of yarn count, weight, thickness, porosity and air permeability using the American Society for Testing and Materials methods cited for each. Fabric counts were measured according to ASTM D3775-98 Standard Test Method for Fabric Count of Woven Fabric and D 3887-96 Standard Specification for Tolerances for Knitted Fabrics. Air permeability (the rate of airflow through a material under a differential pressure between the two fabric surfaces) was measured according to ASTM D 737-96 Standard Test Method for Air Permeability of Textile Fabric using an Air Permeability Tester (Frazier Precision

Instrument Co., Inc., Gaithersburg, MD, USA, No.580). Fabric weight was measured according to ASTM D 3776-96 Standard Test for Mass per Unit Area (Weight) of Fabric for comparison to the published values for each. Fabric thickness was measured according to ASTM D 1777-96. Fabric porosity was defined by ASTM D 4850-99 as the ratio of the volume of air or void contained within the boundaries of a material to the total volume (solid matter plus air or void) expressed as a percentage. The value was calculated using the method described in Guidon et al. (1987).

$$\text{Porosity} = (V/T) \times 100$$

Where V = volume of voids, and T = total volume

4.2.5 Sensory Panel Studies

Sensory panel sessions were conducted in the CFIA Sensory Science Laboratory at the Freshwater Institute in Winnipeg, MB. All experimental procedures and data storage methods for sensory analyses were approved by the Ethics Review Committee of the Faculty of Human Ecology, University of Manitoba. Panelists were required to sign an informed consent form for this work (Appendix A) and all panelists who were part of the final testing were paid an honorarium for their participation. The odor evaluations of fabric swatches were conducted in a standard sensory booth laboratory fitted with individual test booths, controlled lighting, temperature and relative humidity controlled at 22°C and (approximately) 45%, respectively. Test sessions for the fabrics were conducted using red light filters to modify lighting and to disguise visible surface texture differences among the samples.

Thirteen panelists were selected for their ability to correctly identify odor intensities and trained to work with the samples and ballots for these tests. Selection was based on sequential testing using triangle tests as discussed in Study #1 and as shown in Table 3.2 and using the graph in Figure 3.1 for data analysis. Panelists were required to achieve an “accept” for both of the test levels in order to participate in the panel sessions.

Training sessions familiarized the panelists with the test procedures and the samples that they would encounter during the actual panel sessions. Panelists attended a minimum of three training sessions with increasing difficulty of the samples being evaluated.

Each sample was presented as an individual cloth swatch contained in a cassette as shown in Figure 4.2. Both the unexposed and exposed swatches were presented in these containers and each was coded with a three-digit random number. Sets of thirteen swatches, some unexposed and some exposed were presented at each test session using random sample presentation within each session. To evaluate the samples, panelists removed the upper and lower plugs on the cassette and sniffed at the upper port. The plugs were then replaced. Sample sets were prepared fresh each sampling day and were used up to four times in a panel session, after which they were discarded. Odor free water was provided as a rinsing aid for sniffing between samples and panelists were asked to wait 1 minute between evaluations.

The two scaling methods used to measure the intensity of odor perceived in each of the unexposed and exposed cloth swatches were difference-from-control and the labelled magnitude scale. Three replications were performed for each of the scaling methods. The labelled magnitude scale has been used successfully by Zhang et al. (1999) in an initial study of the measurement of environmental malodors, and difference-from-control testing is a standard method used in the analysis of the presence of taints in quality control and in environmental analysis of fish and seafood products exposed to petroleum contamination (Reilly & York, 2001).

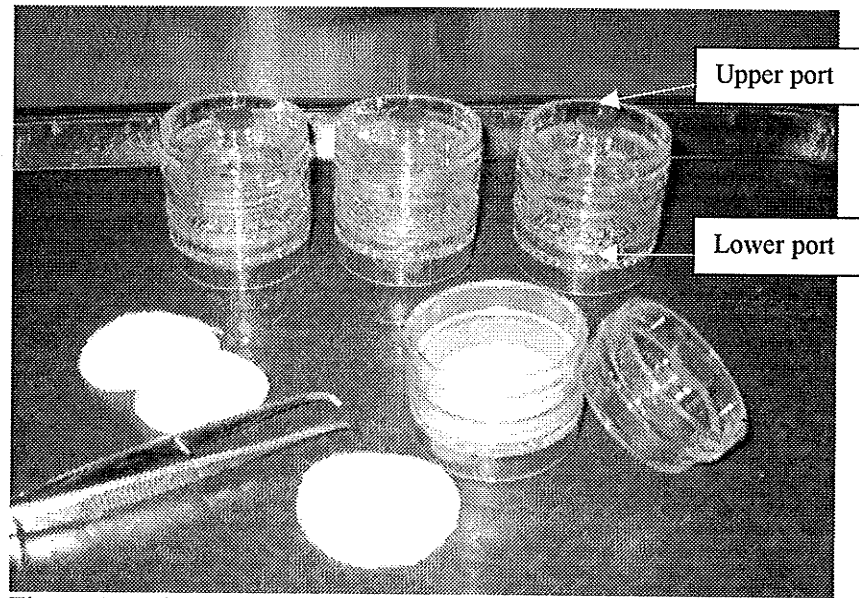


Figure 4.2 Three-piece sampling cassettes used for cloth swatch exposures and for sensory panel presentation.

In the difference-from-control test the panelist was presented with a control sample (unexposed cotton flannel) and asked to rate the amount of difference on either a line or a category scale. For this test, the scaling format used was the 15-cm line scale and data was decoded by measuring the scale with a 150-mm ruler and recording the reading to the nearest whole number. The reference sample was a cassette fitted with an unexposed swatch of cotton flannel. The ballot and panel instructions are shown in Appendix F.

The labeled magnitude scale was developed by Green et al. (1993) and is a line scale with logarithmic spacing for the verbal descriptions. The scale used was 23 cm long with the values with the categories placed at specific points along the line (Zhang et al., 1999). The line scale was decoded using a 300-mm ruler and the reading recorded to the nearest whole number and transformed logarithmically for analysis. The dimensions of the labelled magnitude scale were taken from Green et al. (1993) and were:

% of scale	Descriptor
95.5	strongest imaginable
50.1	very strong
33.1	strong

16.2	moderate
5.8	weak
1.4	barely detectable

The ballot and panel instructions used for this scale are shown in Appendix G. The warm-up sample was a strong sample of the swine odor simulant that was meant to give a very strong reading on the scale.

4.2.6 Electronic Nose Evaluations

There were two stages for the electronic nose analyses: methods development and sample testing. Tests were conducted using an Alpha MOS Fox 3000 Electronic Nose equipped with 12 metal oxide sensors. Prepared samples were placed into a sampling tray for the auto-sampler. Samples were transferred sequentially to the incubator/heating block and gently agitated at constant rpm/directional cycle (500 rpm) to facilitate headspace sample production. In the final test method, the headspace sample (2500 μ l) was drawn into the syringe and transferred to the injection port of the electronic nose. Data collection of sensor response was collected for 120 s followed by 1080 s delay before injection of the next sample. The carrier gas (flow rate maintained at 150 ml per min.) was oxygen/nitrogen at 20% O₂ $\pm$ 1% (i.e. 19.8 to 20.2 % O₂) and with impurities specified as H₂O < 5ppm, C_nH_m < 5ppm, O₂ + N₂ > 99.95%, O₂ = 20% $\pm$ 1%.

Sample preparation for electronic nose analysis using the autosampler consisted of exposing each swatch to the swine odor simulant for 2 minutes at a flow rate of 5 litres/min. The exposed cloth swatches were placed immediately into the 10 ml. auto-sampler vials with the most exposed face of the cloth oriented towards the inside of the vial. These were lidded immediately with magnetic caps lined with silicon/Teflon septa and crimped to seal.

The test conditions used for collection of electronic nose data were as follows:

incubation time:	15 min
incubation temperature:	35, 40, 60°C (also 50, 70 & 80°C)
acquisition time:	2 min

delay time (sensors restored to “zero” state): 18 min

carrier gas flow rate: 150 ml/min

4.2.7 Data Analysis

Data from the difference-from-control analysis (linear scale) were used as the numbers obtained from the assessors. Data from the labelled magnitude scale were normalized as described in Chapter 3.

4.2.7.1 Odor Adsorption for Each Fabric

The data were analyzed using a paired t-test to compare the odor intensity reported for exposed and unexposed swatches for each of the fabrics. Data analyses were performed using a standard computer program (SPSS for Windows Version 10.0.5, SPSS, Inc.)

4.2.7.2 Comparison of Odor Adsorption among Fabrics

The 13 fabrics tested were compared through analysis of variance through the GLM Procedure in SAS Version 8 followed by multiple comparison evaluations using REGWF. This was performed using the data from both scaling systems as difference scores. The results are shown in Table 4.6. The model used contained the variables of panelist, cloth, panelist x cloth interaction.

4.2.7.3 Evaluation of Influence of Physical Attributes on Odor Adsorption by Fabrics

These were evaluated in two ways: first, with all fabrics included, and then, with cottons-only. The data analyses were correlation and multiple regression analysis using SAS Version 8.0

4.2.7.4 Electronic Nose Analyses

Data in the form of sensor responses from the electronic nose were collected and analyzed using AlphaSoft 8.0, the data acquisition and analysis program that controls Alpha MOS Fox 3000 system. This was used for principal component analysis of the exposed versus the unexposed samples. Partial least squares analysis in this system was used to correlated the

sensory and the electronic nose data for the exposed samples. Incubation temperature was evaluated to establish the best test conditions. The results from 35, 40, and 60°C incubation for 15 min were discussed.

4.3 Results and Discussion

4.3.1 Evaluation of Individual Fabrics for their Performance in Odor Adsorption

The first questions to be tested were whether any of the fabrics were able to adsorb the odor and retain it for a sufficient time for sensory testing. If the sensory measurements showed odor adsorption, what did the electronic nose measurements show? How long would the samples last and give stable readings across panelists?

The sensory data from 13 fabrics were used to evaluate the ability of each of the fabrics to adsorb odor from the exposure system. The difference-from-control data were used as numbers (linear scale), and the labelled magnitude scale data were normalized using the method given by Moskowitz & Jacobs (1988). The values for the unexposed and exposed swatches were compared for each panelist/rep pairing using the paired t-test. This method of data analysis was appropriate as the samples were exactly the same except for the odorant exposure used for the exposed samples.

4.3.1.1 Paired t-Tests Of Sensory Odor Intensity Data for Each Fabric

The results of the paired t-tests for each of the scaling methods are shown in Tables 4.3 (difference-from-control) and 4.4 (labelled magnitude scale). In both of the scaling methods tested, assessors were able to detect a significant difference between the exposed and unexposed samples. Both of the methods were able to demonstrate the uptake of odor on all of the fabrics tested. Three fabrics showed the lowest values in both test methods, i.e., linen suiting, cotton terry cloth, and activated carbon cloth. The low values could have been due to lower uptake or to difficulty in the release of the odors. Activated carbon cloth is used to remove odors from environments as a component of air filters and requires higher temperatures to allow odors to be

released. Cotton terry cloth showed a completely different pattern of odor uptake than the other four types of cotton tested. Little odor intensity was perceived in the cotton terry cloth samples. These results allowed Hypotheses I and II to be accepted.

Table 4.3. Mean values for sensory intensity of odor for the fabrics tested using the paired t-test on the results of the difference-from-control test ^a .			
Fabric Description	Intensity difference (Mean) ^b	Standard Deviation	Standard Error of the Mean
cotton - knit	61.4**	33.8	5.6
spun polypropylene	60.1**	30.4	5.1
silk habutae	56.7**	24.5	4.1
Dacron type 54	55.2**	28.4	4.7
spun viscose challis (rayon)	53.7**	33.8	5.6
wool - worsted flannel	53.2**	33.3	5.6
cotton - flannel	50.5**	32.5	5.4
cotton broadcloth	49.3**	36.3	6.0
cotton - twill	46.8**	35.7	6.0
wool challis	35.4**	26.2	4.4
linen - suiting	33.1**	26.5	4.4
cotton - terry cloth	23.3**	26.0	4.3
activated carbon cloth	9.8*	18.5	3.1
*P > 0.01, ** P > 0.001			
^a Fabrics are shown in order of magnitude of the mean odor intensity difference found. ^b n = 33			

Table 4.4. Mean values for sensory intensity of odor for the fabrics tested using the paired t-test on the results of the labeled magnitude scale (log transformed) ^a .			
Fabric Description	Intensity difference (Mean) ^b	Std. Deviation	Std. Error Mean
Cotton - flannel	1.143**	0.510	8.171E-02
cotton broadcloth	1.101**	0.558	8.940E-02
cotton - knit	1.212**	0.478	7.654E-02
cotton - terry cloth	0.749**	0.557	8.919E-02
cotton - twill	0.888**	0.443	7.098E-02
wool - worsted flannel	0.840**	0.455	7.286E-02
wool challis	0.923**	0.503	8.050E-02
silk habutae	0.972**	0.387	6.205E-02
linen - suiting	0.668**	0.539	8.632E-02
spun viscose challis (rayon)	1.165**	0.396	6.347E-02
Dacron type 54	1.235**	0.553	8.864E-02
spun polypropylene	1.186**	0.392	6.281E-02
activated carbon cloth	0.464**	0.552	8.845E-02
*P > 0.01, ** P > 0.001			
^a Fabrics are shown in order of magnitude of the mean odor intensity difference found. ^b n = 33			

As can be seen from these tables and Table 4.5, the two scaling methods did not yield the same rank ordering for the sample fabrics. An analysis of variance was performed (Section 4.3.2) in order to evaluate the differences between the samples and identify any groupings of fabrics which adsorb odors “better”. This was performed and was discussed in the next section.

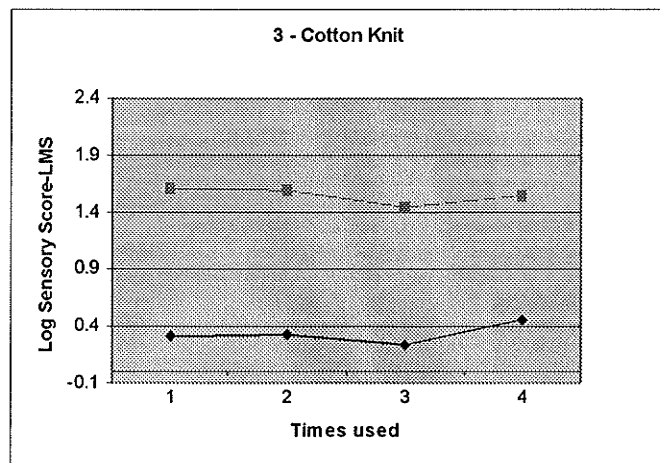
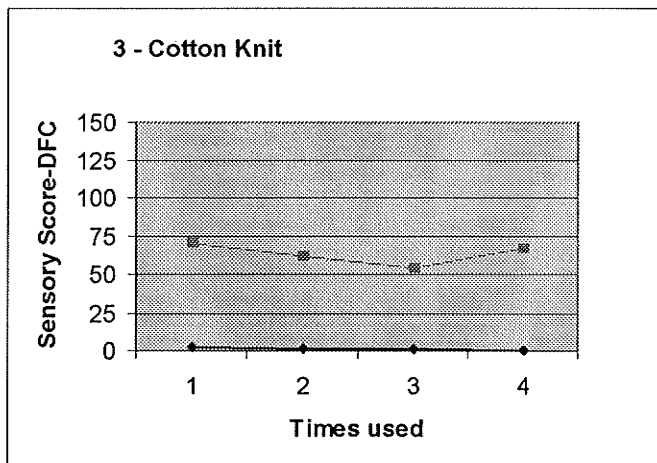
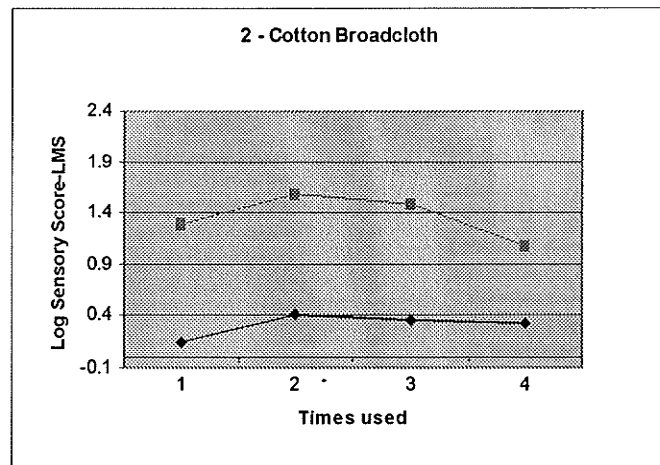
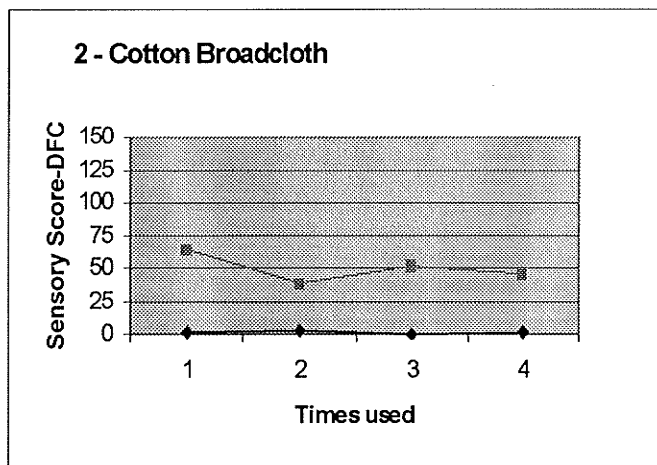
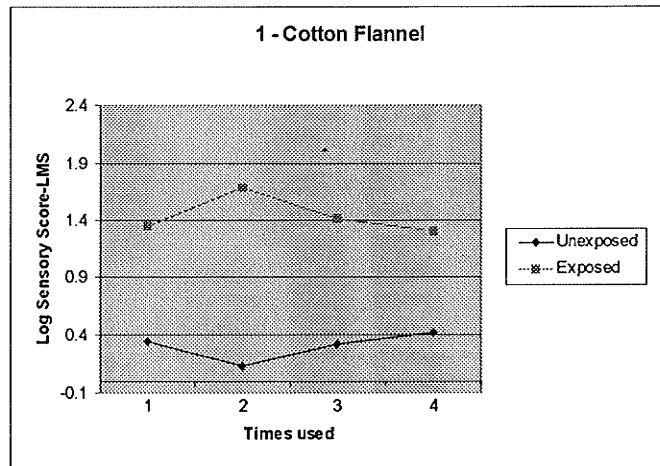
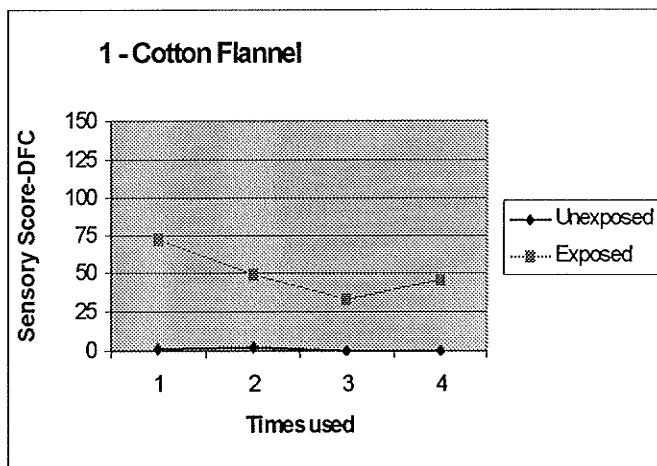
Table 4.5 Summary of the relative “rankings” of the mean odor intensity difference for each of the fabrics tested.				
Fabric Description	Rank Order and Mean Odor Intensity for Difference-from-control Data		Rank Order and Mean Odor Intensity for Labelled Magnitude Scale Data	
cotton - knit	1	61.4**	2	1.212**
spun polypropylene	2	60.1**	3	1.186**
silk habutae	3	56.7**	7	0.972**
Dacron type 54	4	55.2**	1	1.235**
spun viscose challis (rayon)	5	53.7**	4	1.165**
wool - worsted flannel	6	53.2**	10	0.840**
cotton - flannel	7	50.5**	5	1.143**
cotton broadcloth	8	49.3**	6	1.101**
cotton - twill	9	46.8**	9	0.888**
wool challis	10	35.4**	8	0.923**
linen - suiting	11	33.1**	12	0.668**
cotton - terry cloth	12	23.3**	11	0.749**
activated carbon cloth	13	9.8*	13	0.464**

4.3.1.2 Odor Stability or Substantivity during Sensory Panel Testing

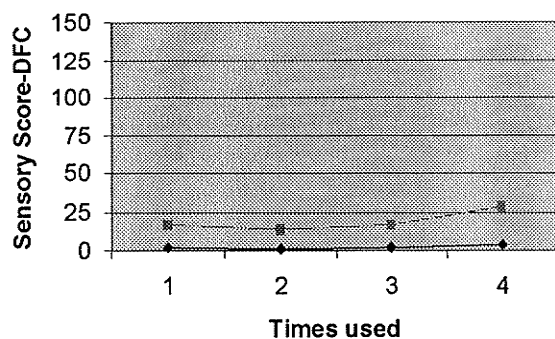
Another factor that must be considered in this type of testing was the stability of the sample during testing; can the cassettes be used repeatedly in evaluating the odor intensity or must they be used only once? The effect of number of times opened was tested by evaluating the average scores assigned to each of the cassettes tested at each testing time and the results are shown in the graphs in Figure 4.3. Each contains a set of graphs for each of the fabrics, with the results from the two scales paired for each of the fabrics. The difference-from-control graphs appear on the left and the labelled magnitude scale graphs on the right. The results from the warm-up sample of exposed cotton flannel is included in Figure 4.4.

These graphs showed the mean sensory score for each "time of use" (i.e., the first, second, third and fourth times each cassette was tested by a panelist). Visual examination of the graphs was the only method available for comparison, given the few data points available for each sample. The results indicated that the samples did not appear to be degraded to any great degree by re-use using the more conservative sampling system. When only the plugs were removed from the cassette, rather than the top half of the unit, the sample was exposed to less room air and appeared to retain its integrity throughout the test period.

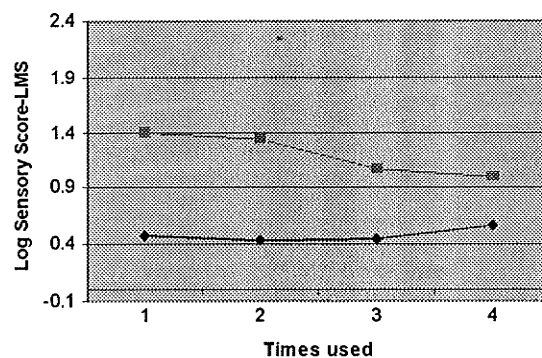
Figure 4.3 Graphs showing the mean sensory score for each “time of use”, i.e. the first, second, third and fourth times each cassette was tested by a panelist. The difference-from-control (DFC) data appears on the left side of the Figure and the labelled magnitude scale (LMS) data on the right side of the Figure.



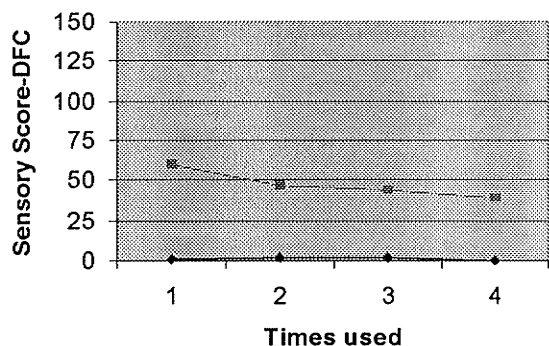
4 - Cotton Terry Cloth



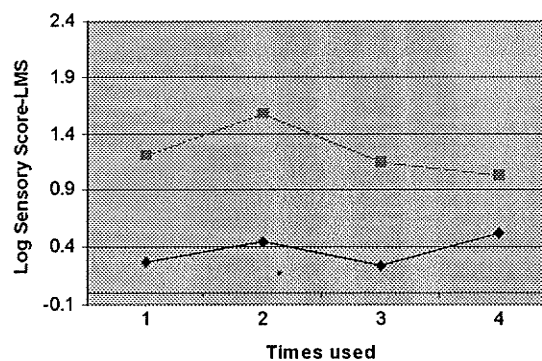
4 - Cotton Terry Cloth



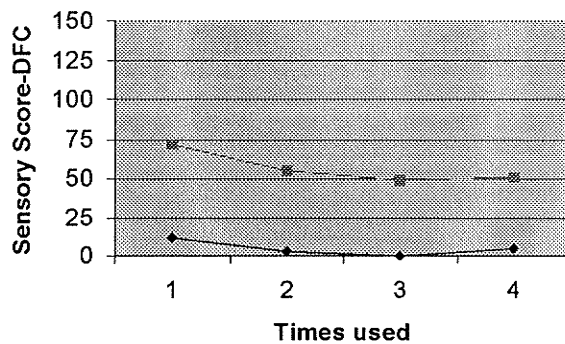
5 - Cotton Twill



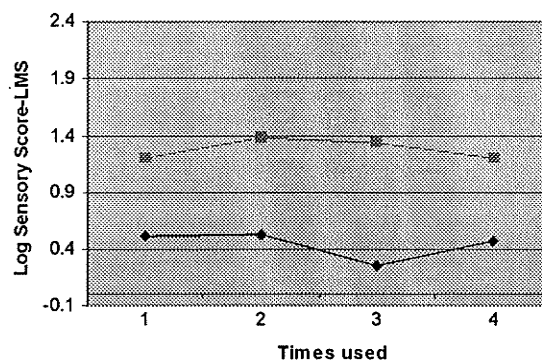
5 - Cotton Twill



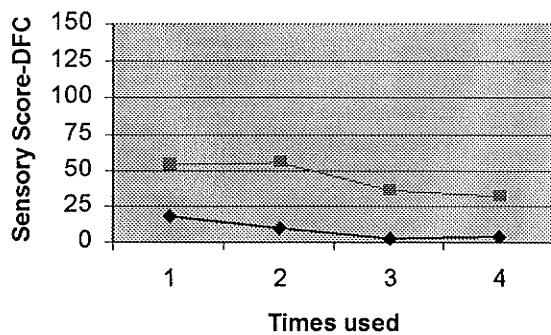
6 - Wool, worsted flannel



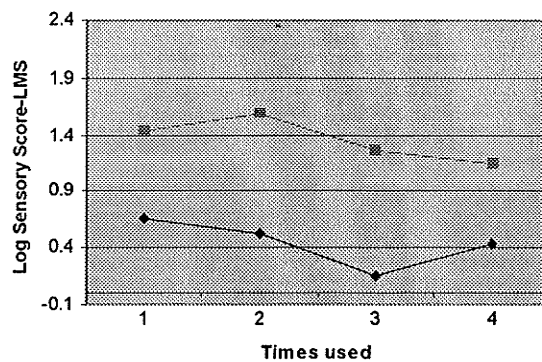
6 - Wool, Worsted Flannel



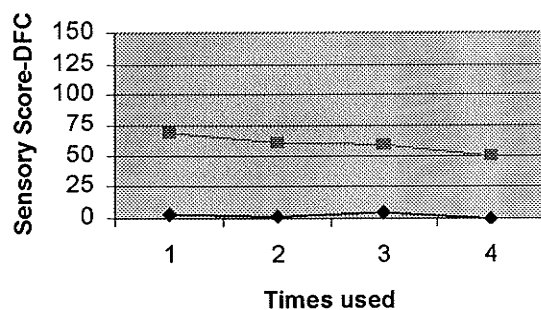
7 - Wool, challis



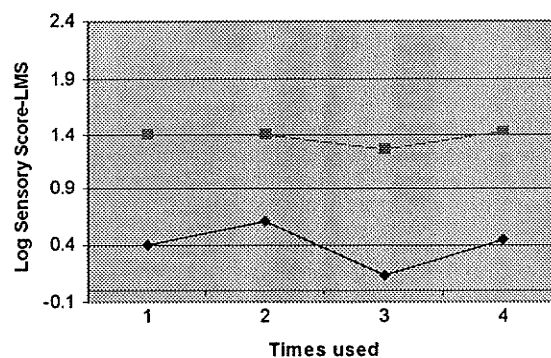
7 - Wool Challis



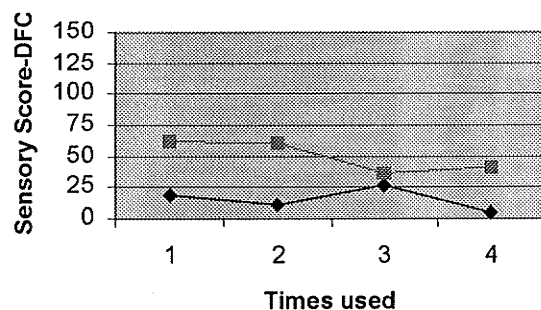
8 - Silk Habutae



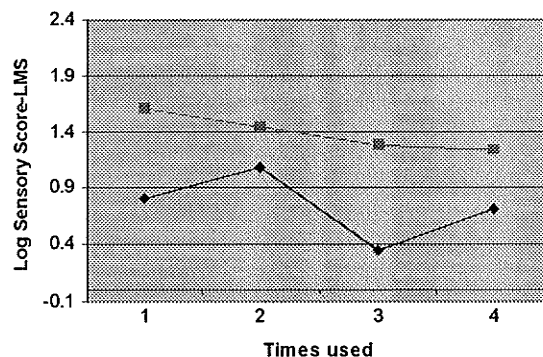
8 - Silk Habutae



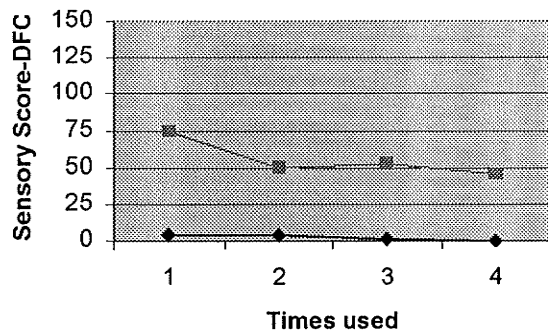
9 - Linen Suiting



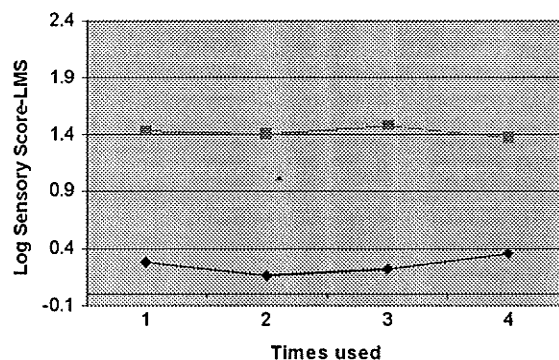
9 - Linen Suiting



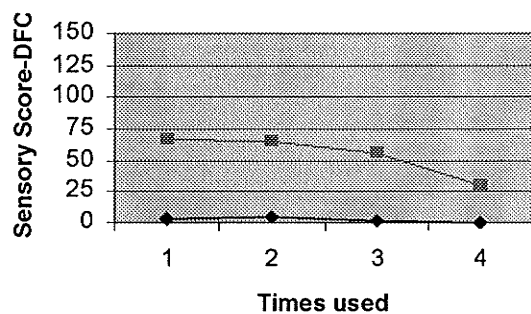
10 - Spun Viscose Challis (rayon)



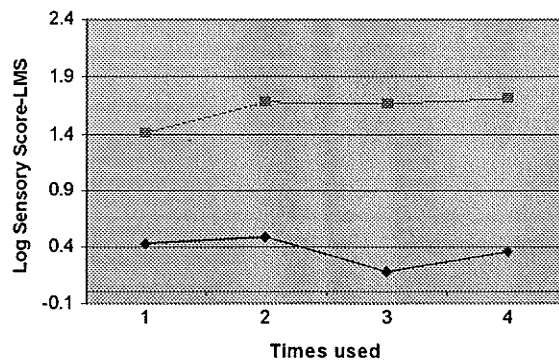
10 - Spun Viscose Challis (rayon)



11 - Dacron type 54



11 - Dacron Type 54



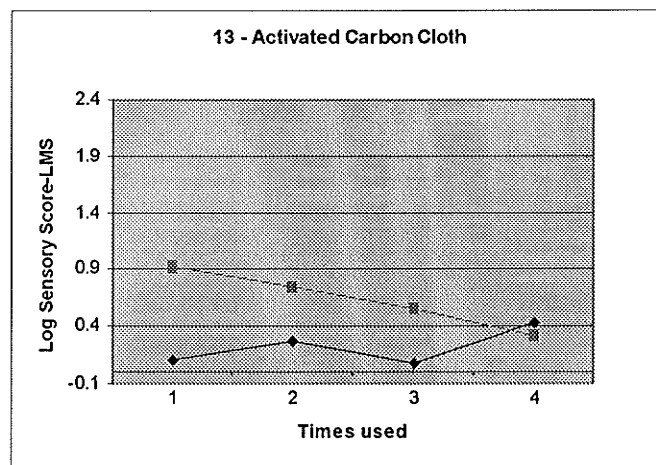
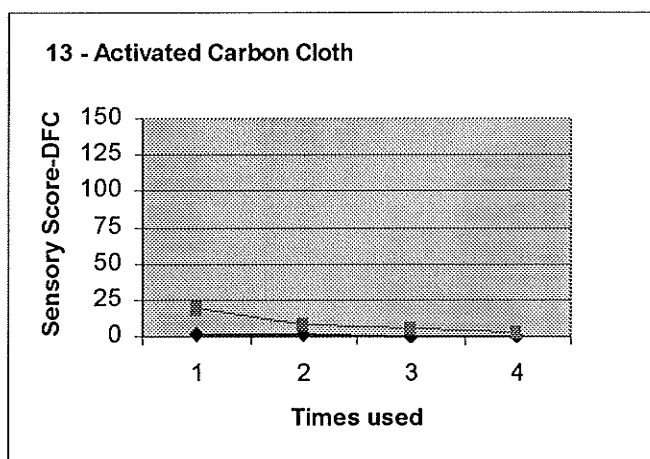
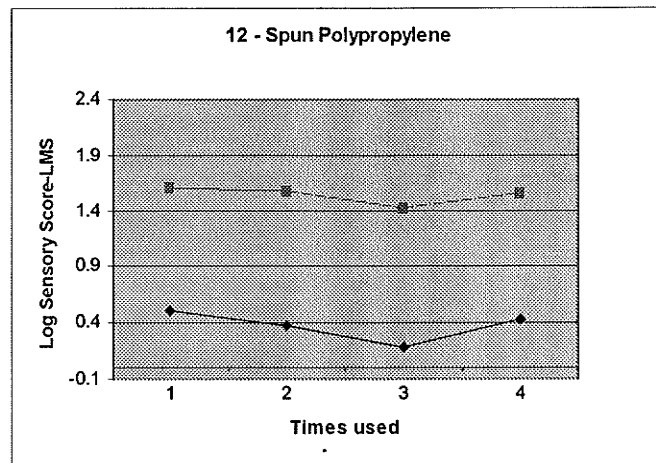
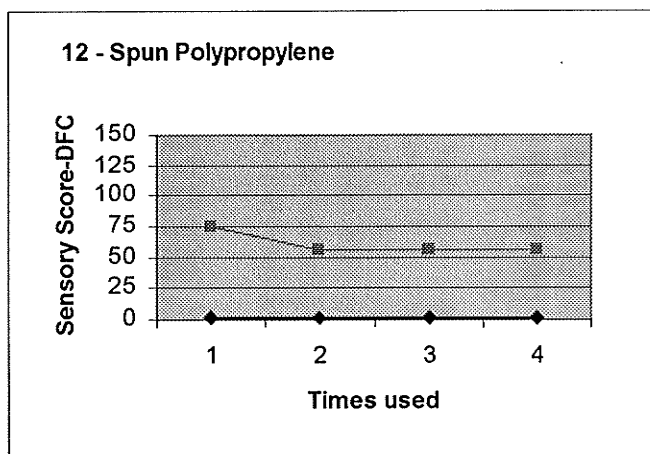
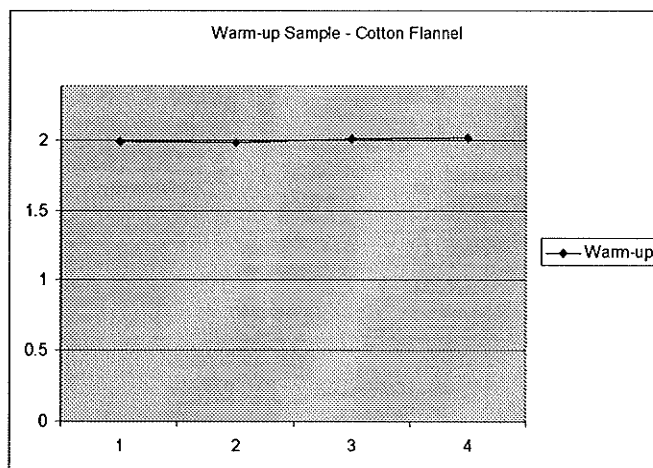


Figure 4.4 Results for warm-up sample, exposed cotton flannel swatch that was used up to four times in labelled magnitude testing.



4.3.1.3 Electronic Nose Evaluation of Odor Properties

The third question in this section is whether the electronic nose would be able to distinguish the same samples that the sensory panel tested. To this end, the electronic nose responses were compared in several ways. The first series of tests on the Alpha MOS Fox 3000 established the ability of the electronic nose to differentiate between the unexposed and exposed swatches. In this case, the results from three of the temperatures tested (35°C, 40°C, and 60°C.) are shown in Appendix H. Each sub-section contains 6 graphs, 3 sets of tracings of the 12 metal oxide sensors over the 2 min acquisition time for an unexposed and an exposed swatch at each of three temperatures and a matching star diagram (referred to as a radar graph in the Alpha MOS AlphaSoft Version 8 software) for each of the tracings.

Both comparisons of the unexposed and exposed swatches showed that the electronic nose was able to distinguish between the two conditions for each of the fabrics. The magnitude of difference between the two conditions was greater at the lower temperatures than the higher ones, presumably because the intrinsic odors of the fibres were influencing the result more at the higher temperature. Both 35°C and 40°C showed good differentiation between the unexposed and exposed swatches. The incubation temperature of 40°C was chosen for the remaining work as a stable operating temperature for the electronic nose system. (Note: This was based on the requirements for optimizing operating parameters for the electronic nose (Alpha MOS, 1999, 2001). The manufacturer's recommended incubation oven temperature for high volatile compounds was 40 to 50°C, which allowed for variations in ambient temperature in the laboratory and met the requirement that the operating temperature of the oven be a least 5°C above the ambient temperature.)

One aspect of the sampling methods that needs to be considered in this analysis is the potential effect of the relative humidity of the samples on the sensor readings. No measurements were made for either relative humidity within the vial or for sample moisture content for the unexposed and exposed samples. There is the potential for sensors to be affected by varying

humidity when, as in this case, the control samples all had a lower relative humidity than the exposed samples. The sensors used in the Fox 3000 system are metal oxide (MOS) sensors and have less sensitivity to humidity than do conducting polymer sensors (Nanto & Stetter, 2003). Work reported by Nagle et al. (2003) compared the results of headspace samples of dilutions of a swine odor simulant solution (similar to the one used above) before and after treatment with a biofilter. Data from a 32-sensor conducting polymer unit equipped with a humidity sensor were compared to measurements of sensory odor intensity, irritation and pleasantness from a trained sensory panel. They found that when the data were compared to the humidity sensor alone, there was very poor correlation between the humidity sensor and the sensory panel responses for all three measurements. When the data were compared to readings from the 32-sensor array, they found good correlation and the values for the correlation coefficients ranged from 0.86 to 0.94. Thus the humidity had little effect on the effectiveness of the evaluation of swine odor in that system. Given that metal oxide sensors are less sensitive to humidity than conducting polymer sensors, there is likely little effect of humidity on the sensor readings for the unexposed and exposed cloth swatches in this study.

Principal component analysis maps comparing unexposed and exposed samples for each of the 13 fabrics tested are given in Appendix I. These showed that the electronic nose could distinguish the presence a difference after exposure to the swine odor simulant for each of the unexposed/exposed fabric pairings. The discrimination index from these maps for each of the fabric pairings is shown in Table 4.6. A discrimination index above 80% was considered to be a good indication of the instrumental discrimination between the sample sets. In this case the discrimination index ranged from 87 to 99%, with 10 of the 14 comparisons shown being 95% and above. Three comparisons were determined for cotton flannel swatches on two different testing days. These were available, as cotton flannel was always included as the standard control sample in the test sets. This showed that all of the fabrics adsorbed and released at least some of

the components of the swine odor simulant during the exposure and testing process and that the Fox 3000 was able to detect this. These results allowed Hypothesis VII to be accepted.

Table 4.6. Discrimination indices for electronic nose comparisons of unexposed and exposed samples for each of the 13 fabrics tested.				
Sample Code (electronic nose)	Fabric Description	Discrimination Index from PCA analysis %		
COT	cotton – flannel, bleached	87	89	95
CTB	cotton broadcloth, bleached, mercerized, combed	97		
CTK	cotton - knit - bleached cotton T-shirt fabric	98		
CTT	cotton - 9.5 oz, bleached terry cloth	94		
CTW	cotton - twill, bleached, mercerized	97		
WOL	wool - worsted flannel	97		
WLC	wool challis	92		
SLK	silk habutae 8 mm	93		
LIN	linen - suiting	98		
RAY	spun viscose challis (rayon)	99		
DAC	Dacron type 54 (disperse dyeable)	96		
PLY	spun polypropylene	96		
ACC	activated carbon cloth	97		

The results of the electronic nose measurements are given in Figures 4.5, 4.6, and 4.7 using the data from the samples tested at an incubation temperature of 40°C and an incubation time of 15 min. The figures contain maps from the principal component analysis (PCA) for the cellulose fibres (5 cotton, 1 linen and 1 rayon) in Figure 4.5, the protein fibres (2 wool samples and 1 silk) in Figure 4.6, and the synthetic fibres (Dacron, polypropylene, rayon, and activated carbon cloth) in Figure 4.7. The groups of exposed and unexposed samples are shown on each of the maps. Each map showed clear distinction between the exposed and unexposed samples for each of the fiber groups. The low discrimination index shown was due to the individual members of each of the two groups mapping with each other (i.e., not showing a difference between the fabrics within the groups). In Figures 4.6 and 4.7, further differences were shown between the unexposed fabrics. In the protein fiber group there were differences between the unexposed

samples of wool and silk as well as between the exposed samples. In the synthetic fibre group, all of the exposed and all of the unexposed samples were differentiated by the electronic nose. This demonstrated the ability of the Alpha MOS Fox 3000 to differentiate between fibre type as well as between the exposed and unexposed state of each of the fabrics. These results allowed Hypothesis VIII to be accepted.

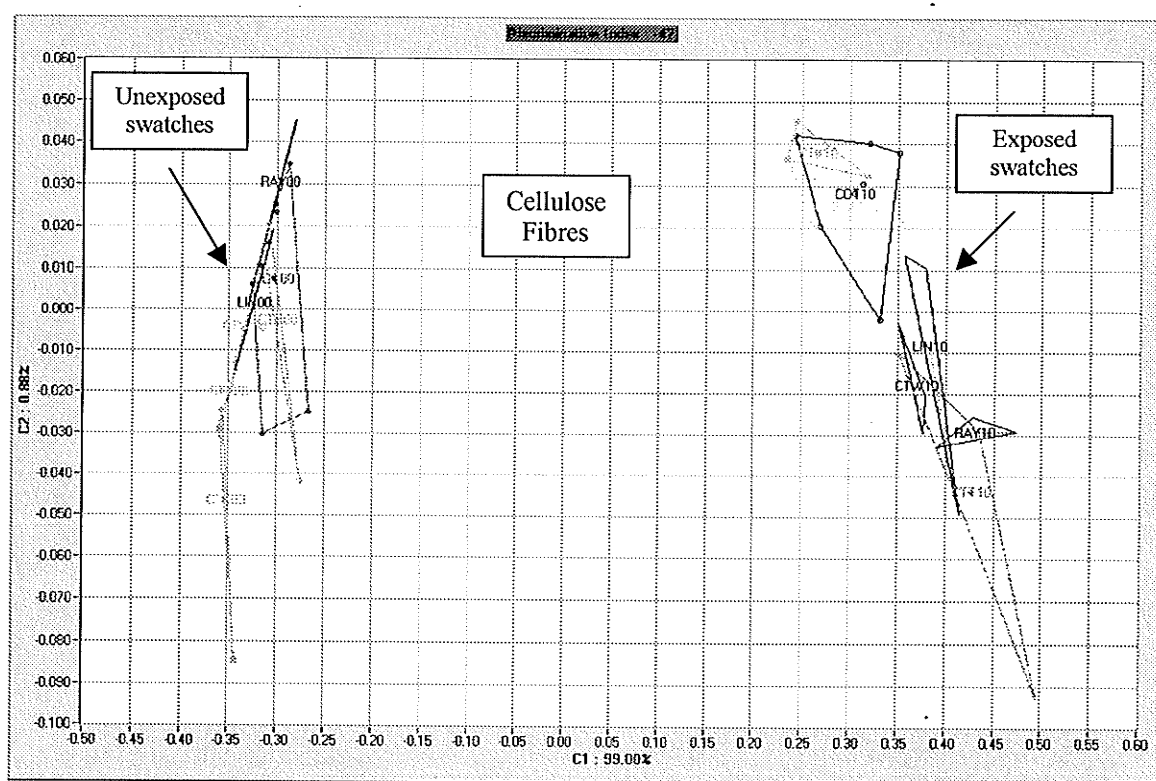


Figure 4.5. Results of PCA maps for electronic nose analyses of fabrics from cellulose fibres. (Discrimination Index (DI) = 47)

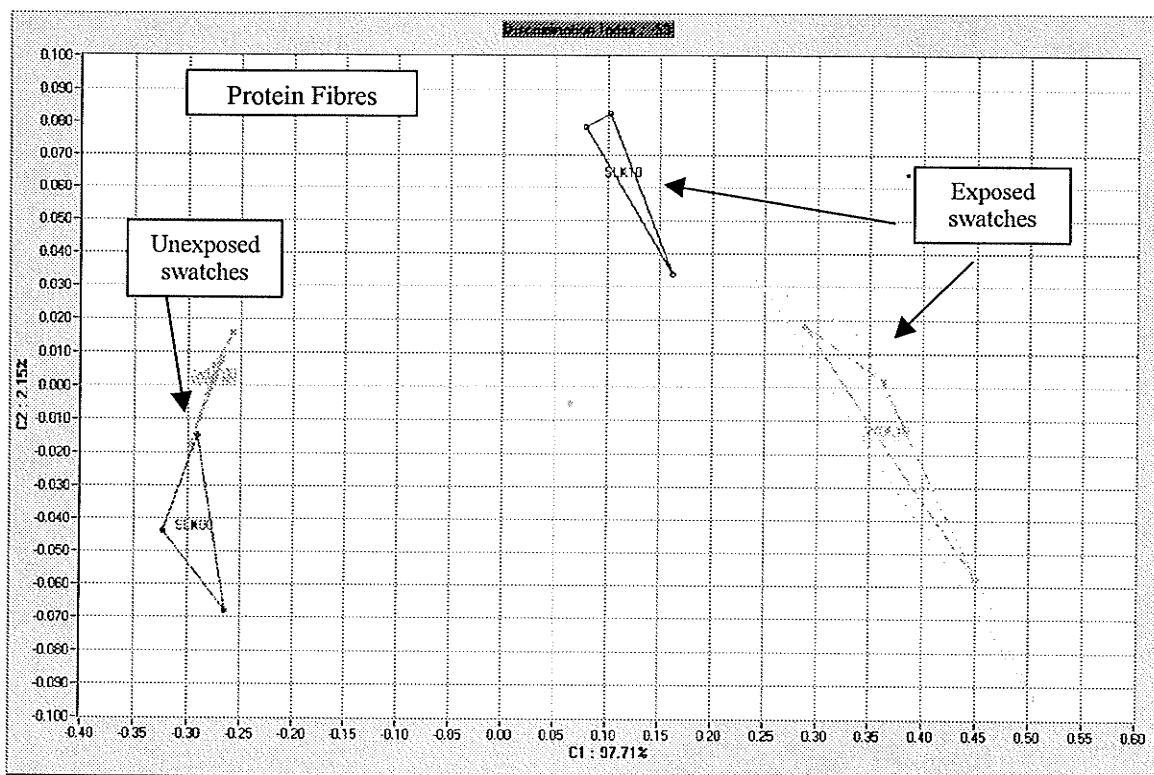


Figure 4.6. Results of PCA maps for electronic nose analyses of fabrics from protein fibres.
DI = 53

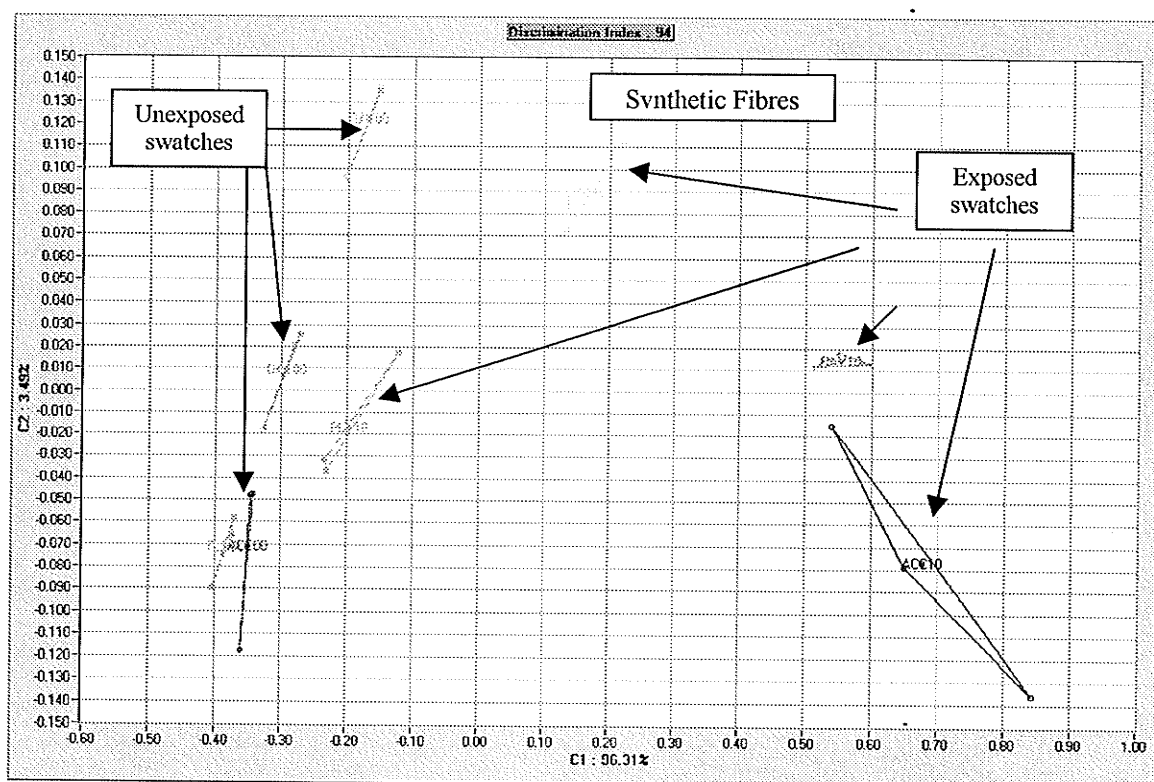


Figure 4.7. Results of PCA maps for electronic nose analyses of fabrics from synthetic fibres.
DI = 94

4.3.2 Comparisons of Odor Adsorption among Fabrics

The results of the evaluations in the previous section showed that each of the fabrics was able to absorb odor to a level that made it measurably different from its unexposed fabric control. The next objective was to identify those fabrics that perform better in odor uptake for this work. Another was to evaluate the scaling methods used to measure the sensory attributes of odor (difference-from-control and labelled magnitude scale). Was one superior in being able to discriminate among the cloth types for their performance?

The experimental design for data collection was based on a repeated measures or within subjects design, also known as a randomized complete block design (Maxwell & Delaney, 1990; Lawless & Heymann, 1999; Tabachnick & Fidel, 1996). This allowed comparisons to be made among the fabrics using analysis of variance methods as well as the within fabrics comparisons used in the previous section. There were advantages to using the within subjects or repeated measures designs. One was the ability to obtain more information for a given cost of data gathering as each subject evaluates each of the samples for the dependent variable rather than providing only one evaluation, as would be the case in between subjects designs. Another advantage was that the comparisons are made within subjects and the variability in individual differences between subjects is removed from the error term.

The 13 fabrics tested were compared for Panelist x Fabric Type through analysis of variance using the GLM Procedure in SAS Version 8 followed by multiple comparison evaluations using Ryan-Einot-Gabriel-Welch multiple F test (REGWF). This analysis was done for each of the scaling methods using 11 panelists, each of whom tested all the fabrics with and without exposure to the swine odor simulant. The values for the analysis of variance were the difference scores for each of the panelists and fabrics. Each data point was calculated by the following formula:

$$\text{difference score} = \text{sensory intensity (SOS-exposed sample)} - \text{sensory intensity (unexposed sample)}.$$

The difference scores were used to analyze the difference-from-control data (linear scale), and the normalized log-transformed difference scores were used for the labelled magnitude scale data (ratio scale). The experiment was designed using a mixed factorial design and all the panelists evaluated all the fabrics and exposure treatments for both scaling systems. The analysis of variance was constructed for each of the data sets using cloth type, panelists and replications as the independent variables.

The results from both scaling methods are shown in Table 4.7. The model contained the variables of panelist, cloth, and panelist x cloth interaction. The model sorted the differences between the fabrics. Table 4.8 shows the differences in fabric groupings for performance based on size of the difference score using REGWF. When the model did not include the interaction term, the groupings were slightly less clear. There was also a difference in the R^2 value for each of the models. When the interaction term was excluded, R^2 was reduced for both scaling methods.

The data showed a significant panelist x cloth interaction. The panelists did not evaluate all of the same samples in the same way. While the samples were masked by the use of red lights, which made the texture differences among the samples difficult to see, there may have been some effect from the visual cues. The color of the activated carbon cloth could not be masked, as it was carbon black. The data was analyzed as cloth type x panelist with interaction, for cloth type x panelist without interaction, and as cloth type x panelist without two of the fabrics. The two omitted were cotton terry cloth and activated carbon cloth, based on examination of the box plot function with outliers far outside the range of the rest of the readings for those samples.

Table 4.7 ANOVA results for sensory means of odor uptake by fabric swatches					
Source	df	SS	F	Pr > F	R ²
Labelled magnitude scale data					
Panelist	10	87.1741	52.36	<.0001	0.7469 (= 0.5925 without interactions)
Cloth	12	24.3081	12.17	<.0001	
Panelist x Cloth	120	29.0665	1.45	0.0060	
Error	286	47.6137			
Difference-from-control data					
Panelist	10	153172.3124	30.58	<.0001	0.7024 (= 0.5174 without interactions)
Cloth	12	95863.4452	15.95	<.0001	
Panelist x Cloth	120	89016.6573	1.48	0.0042	
Error	286	143262.6667			

There were three replications in each of the test series and the effect of including Replications in the ANOVA was evaluated in the difference-from-control and labelled magnitude scale data by adding this factor into the model. While this factor was significant, with $F(2 \text{ and } 240) = 7.66$, $p = 0.0006$, little useful information was added by including it in the analysis. The R^2 value was 0.7191 for difference-from-control, meaning that the inclusion of this factor only explained 1.67% more of the variability in the data. For the labelled magnitude scale data, these values were $F(2 \text{ and } 284) = 4.00$, $p = 0.0194$. The R^2 value was 0.7539 for the labelled magnitude scale data, meaning that the inclusion of this factor only explained 0.70% more of the variability in the data. Given that so little was added by including replication in the ANOVA, it was excluded from further analyses of both sets of data.

Table 4.8 shows REGWF multiple range groupings of the sensory means for each of the scaling methods, difference-from-control and labelled magnitude scale tests. There was no discernible pattern shown in Table 4.8 that can be related to the fibre type or chemical nature of the fibre shown in Table 4.9. Cellulose fabrics performed as both the best (cotton knit, CTK) and worst (cotton terry cloth, CTT) in adsorbing and releasing odor in the test conditions. These two cottons were standard fabrics, made from untreated cotton fibres, had no applied finishes, and were purchased from the same manufacturer. The chemical nature of the surface of the fabric did not form a pattern either, as the best performers in the difference-from-control test were a

cellulose fabric and a synthetic fabric, one hydrophilic and the other hydrophobic. The reason for this was not clear. However the results show that all the fabrics retained odor to some degree when exposed to the swine odor simulant. Two fabrics, linen suiting (LIN) and cotton terry cloth (CTT), retained only a very low level of odor compared to the other fabrics. The third fabric which did not appear to do well as a laboratory sampling fabric was activated carbon cloth (ACC); however, it is designed to adsorb and retain odors, so may still be of use when a suitable protocol for releasing the odors is established. These results allowed Hypotheses III and IV to be accepted.

Table 4.8. The REGWF groupings for cloth swatch odor pick-up intensity for each of the two scaling methods using different models to evaluate the data.			
Model with the interaction term.		Model without interaction term, no replication effect	
Difference-from-control Test	Labelled Magnitude Scale	Difference-from-control Test	Labelled Magnitude Scale
CTK ^a	CTK ^a	CTK ^a	CTK ^a
PLY ^a	COT ^{ab}	PLY ^a	COT ^a
SLK ^a	RAY ^{ab}	SLK ^a	RAY ^{ab}
DAC ^a	DAC ^{ab}	DAC ^a	DAC ^{ab}
WOL ^{ab}	PLY ^{ab}	WOL ^a	PLY ^{ab}
RAY ^{ab}	CTB ^{abc}	RAY ^{ab}	CTB ^{abc}
COT ^{abc}	SLK ^{abcd}	COT ^{ab}	SLK ^{abcd}
CTW ^{abc}	WLC ^{bcd}	CTW ^{abc}	WLC ^{abcd}
CTB ^{bc}	CTW ^{cde}	CTB ^{abc}	CTW ^{bcd}
WLC ^{bc}	WOL ^{cde}	WLC ^{bcd}	WOL ^{cde}
LIN ^c	CTT ^{de}	LIN ^{cd}	CTT ^d
CTT ^d	LIN ^{ef}	CTT ^{cde}	LIN ^{de}
ACC ^d	ACC ^f	ACC ^{de}	ACC ^e
¹ Samples with the same letter are not significantly different at $\alpha = 0.05$			

Table 4.9 Chemical nature of the surfaces of the fabrics used.			
Fabric	Fabric type		
		Hydrophilic = “+”	Hydrophobic = “-”
CTK	Cellulose	“+”	
PLY	Synthetic		“-”
SLK	Protein	“+”	
DAC	Synthetic		“-”
WOL	Protein	“+”	
RAY	Cellulose (modified) Synthetic	“+”	
COT	Cellulose	“+”	
CTW	Cellulose	“+”	
CTB	Cellulose	“+”	
WLC	Protein	“+”	
LIN	Cellulose	“+”	
CTT	Cellulose	“+”	
ACC	Cellulose (modified) Synthetic	“+”	
This information is taken from Gohl and Vilensky (1983) pp210-211.			

Given the success of adsorbing odor from a large range of fabrics, other factors were considered, which would affect the choice of fabrics for field sampling. These were the physical handling problems that occurred during cloth swatch preparation and testing. The cotton knit (CTK), which seemed to be the best performer for adsorbing odor, was also the most difficult fabric to work with for swatch preparation. It was very thin and being a single knit, tends to roll, a tendency exaggerated in the small swatches used. It was impossible to make it lie flat in the cassettes and to orient it in the vials used for electronic nose testing. Therefore, the evenness of exposure to the odorants could not be controlled. It was also extremely difficult to cut. This combination of factors was the basis of eliminating it from further testing in the remainder of the work. In addition, the various types of cotton fabrics were spread throughout the range of sensory means, not grouped in one range of numbers. The different forms of cotton fabrics did not behave consistently, and there might be something in the physical properties measured that would help to distinguish them and provide guidance for selection of optimum fabrics for swatch use.

Table 4.10 shows the different groupings for the panelists for the different scales. The data for the two methods were not compared statistically; however, both methods showed a significant panelist x cloth effect in the analysis. This was likely more of an artifact for the fact

that while the panelists were selected and trained to the specific task, they could not be considered to be an expert panel. This would result in greater variability in the responses given. This effect was likely panel specific and can be removed in further testing through extended training sessions prior to the study. The presence of this greater variability in the selected, trained panel does not negate the usefulness of the results. This was demonstrated in a tainting study conducted by this writer in which a community panel familiar with the taint in question was compared to the performance of a true product expert, a trained validated expert in fish inspection. The taint was pulp and paper mill effluent and the species subjected to the taint were a fish called eulachon, which pass the outflow of the mill on the Kitimat River during their spring spawning run. Both wild caught, tainted and clear, and laboratory-tainted samples were evaluated by the community panel and by the expert using the difference-from-control methodology. The results showed that while the community panel showed mean values for taint level with high standard deviations, the means were actually the same as those produced by the expert assessor (who showed very low standard deviations) (York and Boyd, 1999, unpublished data).

Table 4.10. The REGWF groupings for panelists (shown by Identification Number) assessing cloth swatch odor pick-up intensity for each of the two scaling methods using different models to evaluate the data*.			
Model with interaction term, no replication effect – panelists		Model without interaction term, no replication effect – panelists	
Difference-from-control Test	Labelled Magnitude Scale	Difference-from-control Test	Labelled Magnitude Scale
3 ^a	3 ^a	3 ^a	3 ^a
1 ^{ab}	4 ^a	1 ^{ab}	4 ^a
8 ^{bc}	9 ^b	8 ^{bc}	9 ^b
5 ^{bc}	5 ^{bc}	5 ^{bc}	5 ^{bc}
2 ^c	8 ^c	2 ^{cd}	8 ^c
4 ^c	11 ^c	4 ^{cd}	11 ^c
7 ^d	13 ^c	7 ^{de}	13 ^c
9 ^d	10 ^{cd}	9 ^e	10 ^c
13 ^d	1 ^d	13 ^e	1 ^d
10 ^d	2 ^d	10 ^e	2 ^d
11 ^d	7 ^d	11 ^e	7 ^d
*Panelists with the same superscript are not significantly different in response from each other at $\alpha = 0.05$.			

A preliminary examination of the data through the box plot function showed a difference in the cotton terry cloth (CTT) and activated carbon cloth (ACC) with outliers far outside the range of the rest of the readings for those samples. Outliers were also present for wool challis (WLC). The behaviour of the first two, cotton terry cloth and activated carbon cloth, relative to the retention of odor made it reasonable to exclude these from the analysis and to examine the results again. These two fabrics showed a much lower release of odors into the sample container, although as is seen by both the paired t-test and the electronic nose analyses, both did adsorb some odor. This would be expected in the case of activated carbon cloth, which is produced to adsorb and not release odors. However, why this happens for cotton terry cloth was not clear, as it is the same fibre as the best performer, cotton knit.

To see if the extreme means had an effect on the results and on the groupings of the other fabrics, the cotton terry cloth and activated carbon cloth were omitted, and the analyses run again. (Note that wool challis also showed outliers, but since it was in the middle of the grouping for odor uptake, it was left in the analysis.) The results are shown in Table 4.11. When this analysis with 11 fabrics was compared to the analysis of the 13 fabrics, there was no advantage in removing the two fabrics from the analysis. In fact, the value of R^2 was almost unchanged for the labelled magnitude scale data (from 0.7469 reduced to 0.7465) and lower for the difference-from-control data (0.7024 reduced to 0.6544). As with the first analysis of data, the replication effect added little information to the analysis.

Ultimately, both scaling methods were able to discriminate among fabrics. There were significant panelists by cloth type interactions. Panel training may have had some effect on the analysis, as this was a selected trained panel, but would not be considered to be an expert panel. A less expert panel is subject to greater variability in the assigned values from session to session, but testing this would require a repeat of the study with a different sensory panel.

Table 4.11 ANOVA results for fabric swatches cotton terry cloth and activated carbon cloth removed.					
Source	df	SS	F	Pr > F	R ²
Labelled Magnitude Scale Data					
Panelist	10	75.2463	48.58	<.0001	0.7465 (= 0.5966 without interactions)
Cloth	10	12.9627	8.37	<.0001	
Panelist x Cloth	100	22.1542	1.43	0.0140	
Error	242	37.4799			
Difference-From-Control Data					
Panelist	10	146491.0799	27.08	<.0001	0.6544' (= 0.4587 without interactions)
Cloth	10	27289.0193	5.04	<.0001	
Panelist x Cloth	100	74174.9807	1.37	0.0265	
Error	242	130931.3333			

4.3.3 The Relationships of Physical Properties and Odor Uptake Measured by Sensory Panels and by the Electronic Nose

There were differences in the way that the fabrics performed for odor adsorption, which did not appear to be governed by the chemical nature of the surface of the fabric. Given that, one of the next questions is then, were there attributes of the physical nature of the fabrics that enhance their adsorption of odor?

The results of the physical measurements made to characterize the basic properties of the fabrics are shown in Table 4.12. These include fabric weight, yarn counts for both warp and weft, thickness, density, porosity, and air permeability. It should be noted that all physical measurements were done on new fabrics according to the ASTM methods for each given in Section 4.2.4. These data allowed the relationship of the physical attributes of all of the fabrics to the sensory scores for odor uptake to be evaluated. Furthermore, because there were five different forms of cotton used in the study, varying from the highest to one of the lowest sensory scores (for cotton terry cloth) the role of the physical attributes within a fibre group can be examined. The combination of the physical and sensory data for each of the fabrics and for the two scaling methods allowed statistical analyses of any relationships of physical measurements to the sensory measurements of odor adsorption.

The relationship of physical attributes to sensory scores was evaluated in two ways – first with all fabrics included and then with cottons only, as there were 5 different cotton samples in the study. The data analysis was correlation and regression analysis using SAS Version 8.0.

Table 4.12. Physical measurements on the 13 fabrics tested for odor uptake.

Fabric Description	Weave Structure & Surface		Yarn counts (per inch) ¹		Weight (g/m ²)			Thickness ³ (inches)	Density ⁴ (g/cm ³)	Porosity ⁵ (% air)	Air Permeability ⁶ (cc/cm ²)
			warp	weft	nominative	measured	% difference				
cotton - flannel, bleached	plain	napped	48	46	122	129.25	6%	0.0386	1.55	91.489	73.57
cotton broadcloth,	plain	smooth	141	69	120	120.41	0%	0.01226	1.55	75.052	30.48
cotton - knit	knit	smooth	79	n/a	102	140.14	37%	0.0238	1.55	85.065	101.29
cotton - terry cloth	pile	looped pile	63	36	295	362.48	23%	0.0980	1.55	90.603	84.85
cotton - twill	Twill	smooth	116	84	186	196.02	5%	0.0210	1.55	76.239	9.00
wool - worsted flannel	Twill	smooth	53	42	173	168.95	-2%	0.0265	1.31	80.857	55.59
wool challis	Plain	smooth	55	57	107	121.33	13%	0.0212	1.31	82.784	95.61
silk habutae	Plain	smooth	130	117	36	34.52	-4%	0.0053	1.33	80.872	80.92
linen - suiting	plain	smooth	42	36	218	236.56	9%	0.0205	1.5	69.764	49.32
spun viscose challis (rayon)	plain	smooth	69	55	138	122.65	-11%	0.0165	1.515	80.686	109.69
Dacron type 54	plain	smooth	53	55	126	125.85	0%	0.0184	1.38	80.536	104.07
spun polypropylene	plain	smooth	41	33	170	166.46	-2%	0.0270	0.9	73.063	30.67
activated carbon cloth	plain	smooth	33	30	n/a	158.61	n/a	0.0256	2.33	89.551	123.33

¹ ASTM D3775-98 (woven fabric) and D 3887-96 (knit fabric)
² ASTM D 3776-96
³ ASTM D 1777-96
⁴ standard table of reference
⁵ ASTM D 4850-99
⁶ ASTM D 737-96

4.3.3.1 Sensory Panel Assessments of All Fabrics vs Physical Properties

As a first step in this analysis, the correlation (R^2) for the physical measurements were calculated so that highly correlated attributes would not be used in the subsequent regression analyses. The results of these correlations are shown in Table 4.13.

Table 4.13 Correlation coefficients (R) for the various physical measurements performed on the 13 fabrics used for odor sampling.					
	Weight	Thickness	Density	Porosity	Air Permeability
Weight	1.00	0.812	0.107	0.053	-0.166
Thickness		1.00	0.096	0.536	0.094
Density			1.00	0.472	0.440
Porosity				1.00	0.598
Air Permeability					1.00
Note: The mean value of each physical attribute for each of the fabrics was used to calculate these correlations, sample size = 13.					

Porosity was eliminated on the first analysis with the labelled magnitude scale data, as it proved to be a very poor predictor when it was included instead of density. The adjusted R^2 for sensory score related to thickness, porosity and air permeability was only 0.1855. Density was used in the final analysis with the following results.

When the regression was calculated with the labelled magnitude scale data for all fabrics, the result was:

$$\text{Sensory score (as log value)} = 1.78229 - 0.00120 (\text{fabric weight}) - 0.45691 (\text{density}) + 0.00090040 (\text{air permeability})$$

and the relationship explained 46.51% of the variability in the scores. (adjusted $R^2 = 0.4651$).

When the regression was calculated with the difference-from-control data for all fabrics, the result was:

$$\text{Sensory score} = 108.21457 - 0.09622 (\text{fabric weight}) - 29.66835 (\text{density}) - 0.04294 (\text{air permeability})$$

and the relationship explained 66.94% of the variability in the scores. (adjusted $R^2 = 0.6694$).

The lower value for the adjusted R^2 for all fabrics compared to the cottons only might indicate that when a variety of fibres are included in the analysis, there were other factors connected with their surface chemistry, which might add information to the prediction equation. This information was not part of this study.

4.3.3.2 Sensory Panel Assessments For Cottons Only vs Physical Properties

The value for density was omitted here it is constant for the fibre and is thus the same for all the samples. As such, it provides no information in the correlation. As a first step in this analysis, the correlation (R^2) for the remaining physical measurements were calculated so that highly correlated attributes would not be used in the subsequent regression analyses. The results of these correlations are shown in Table 4.14.

Table 4.14 Correlation coefficients (R) for the various physical measurements performed on the five cotton fabrics for odor sampling.				
	Weight	Thickness	Porosity	Air Permeability
Weight	1.00	0.881	0.228	0.150
Thickness		1.00	0.636	0.470
Porosity			1.00	0.792
Air Permeability				1.00

When the regression was calculated with the labelled magnitude scale data for cottons only, the result was:

$$\text{Sensory score (as log value)} = 1.24075 - 0.00187 (\text{fabric weight}) + 0.00215 (\text{air permeability})$$

and the relationship explained 99.24% of the variability in the scores. (adjusted $R^2 = 0.9924$).

When the regression was calculated with the difference-from-control data for cottons only, the result was:

$$\text{Sensory score} = 66.06803 - 0.12633 (\text{fabric weight}) + 0.05752 (\text{air permeability})$$

and the relationship explained 83.75% of the variability in the scores. (adjusted $R^2 = 0.8375$). This indicated that decreased fabric weight and increased air permeability were associated with increased odor adsorption. These results allowed Hypotheses V and VI to be rejected for the multiple regression relationship across all fabrics to be rejected and the multiple regression relationship for the group of cotton fabrics to be accepted.

4.3.3.3 Electronic Nose Analyses of Odor Adsorption vs Physical Properties

Another way of examining the data was through the electronic nose analyses of the samples and the way in which the electronic nose was able to differentiate among the unexposed and exposed fabrics. The fabric attributes that were shown to be associated with odor uptake when all fabrics were considered were fabric weight, density and air permeability. When only the cotton samples were tested, the two attributes that were important were fabric weight and air permeability. In the light of this, Figure 4.11 begins a series of graphs that show the relationships between the physical properties for each of the fabrics (Table 4.12). The physical measurements that were obtained for each of the tested fabrics were weight (g/m^2), thickness (inches), porosity (% air in a given volume of fabric), density and air permeability (cc/cm^2). Each of these properties was evaluated for the existence of a relationship using the three groupings (protein fibres, cellulose fibres and synthetic fibres) using the linear format of the PLS analysis in AlphaSoft Version 8.0. The treatment conditions for the analysis in the Alpha MOS Fox 3000 were standardized here to incubation at 40°C. for 15 min before drawing the 2500 μl headspace sample.

The correlation coefficients from these graphs are summarized in Table 4.15, which also acts as a “directory” to associate the resulting correlation coefficient and the source graph. For these analyses, the fabrics were grouped into appropriate subgroups to evaluate relationships to the electronic nose sensor readings. These groups were; all protein fibres (three fabrics), all cellulose fibres (eight fabrics), cottons only (five fabrics), cottons plus linen (six fabrics), cottons

plus linen and rayon (a modified cellulose) (seven fabrics), and all synthetic fibres (4 fabrics).

Analyses were also done using all fabrics (13 fabrics) and all fabrics minus activated carbon cloth (12 fabrics).

Table 4.15. Relationships of the physical attributes of the fabrics tested with the electronic nose responses for various combinations of the fabrics used in the study. The relationship is characterized by the correlation coefficient from the SSC algorithm and the corresponding Figure number is identified for each of the graphs.

Attribute		Fabric combination tested ^a							
		Protein (three fabrics)	Cellulose				Synthetic (four fabrics)	All fabrics (13 fabrics)	All fabrics minus ACC (12 fabrics)
			All (eight fabrics)	Cotton only (five fabrics)	Cotton plus linen (six fabrics)	Cotton plus linen & rayon (seven fabrics)			
Fabric Weight	R*	0.8895	0.6080	0.8679	0.8609	0.7284	0.9077	0.5570	0.6240
	Figure #	4.8	4.9	4.10	4.11	4.12	4.13	4.14	4.15
Density	R*							0.7492	0.8728
	Figure #							4.16	4.17
Air Permeability	R*	0.8580	0.6282	0.6013	0.5781	0.5646	0.9778	0.3270	0.3413
	Figure #	4.18	4.19	4.20	4.21	4.22	4.23		
Porosity	R*	0.9068	0.6135	0.6489	0.7097	0.6422	0.9270	0.4038	0.3774
	Figure #	4.24	4.25	4.26	4.27	4.28	4.29		
Thick-ness	R*	0.9135	0.5073	0.7853	0.7714	0.6475	0.8796	0.3673	0.4320
	Figure #	4.30	4.31	4.32	4.33	4.34	4.35		

* R = correlation coefficient from Sensory Score Correlation PLS analysis through AlphaSoft 8.0

Note: Graphs with a correlation coefficient less than 0.5 are not shown.

^a Some fabrics have been included in more than one group. Rayon is a modified cellulose and may be considered both a cellulose and a synthetic. Activated carbon cloth is manufactured from rayon, and was included in the cellulose group as well as in the synthetic group.

The results in Table 4.15 indicated certain patterns when the correlation coefficients for the different groupings were examined, and when only $R > 0.85$ was designated as an indicator of the relationships.

1. Fabric weight was best correlated with the sensor readings for the protein fibre group, for the cottons only and the cottons plus linen group, and for the synthetic fibre group.
2. Density was best correlated with the sensory readings for the group of all fibres used minus activated carbon.
3. Air permeability was best correlated with the sensor readings for the protein fibre group and the synthetic fibre group.
4. Porosity was best correlated with the sensor readings for the protein fibre group and the synthetic fibre group.
5. Thickness was best correlated with the sensor readings for the protein fibre group and the synthetic fibre group.

These results allowed Hypothesis IX to be accepted for the group of 3 protein fibres and for the group of 4 synthetic fibres in Table 4.15 for the properties of fabric weight, fabric thickness, air permeability and porosity. The detailed results for these correlations are given in the following SSC graphs; with Figures 4.8 to 4.15 showing the linear regression analyses of sensor readings and fabric weight, Figures 4.16 and 4.17 showing the linear regression analyses with density, Figures 4.18 to 4.23 showing the linear regression analyses with fabric air permeability, Figures 4.24 to 4.29 showing the linear regression analyses with fabric porosity, and Figures 4.30 to 4.35 showing the linear regression with fabric thickness. The Table 4.15 shows the Figure number associated with each of the correlation coefficients.

4.3.3.3.1 Graphs Relating Fabric Weight and Sensor Signal Intensity

The effect of fabric weight (here as g/m²) effectively measures the amount of fabric present in the cassette - as the diameter of the swatch is constant for all the tests.

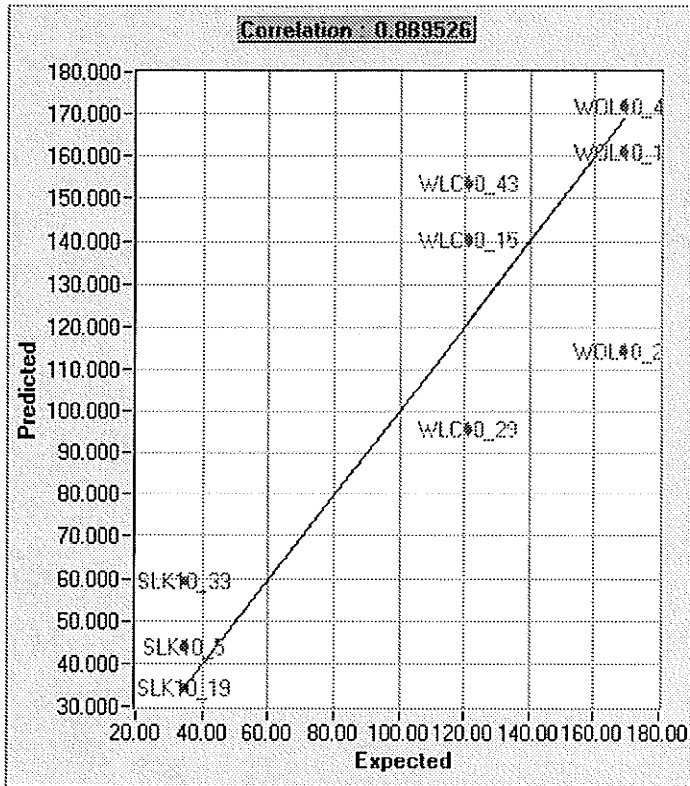


Figure 4.8 Linear regression (SSC) for Protein Fibres vs Fabric weight

Only three fabrics were used here, but there appears to be some association with the amount of fibre present for the protein fibres and the intensity of the sensor response.

Wool flannel
Wool challis
Silk

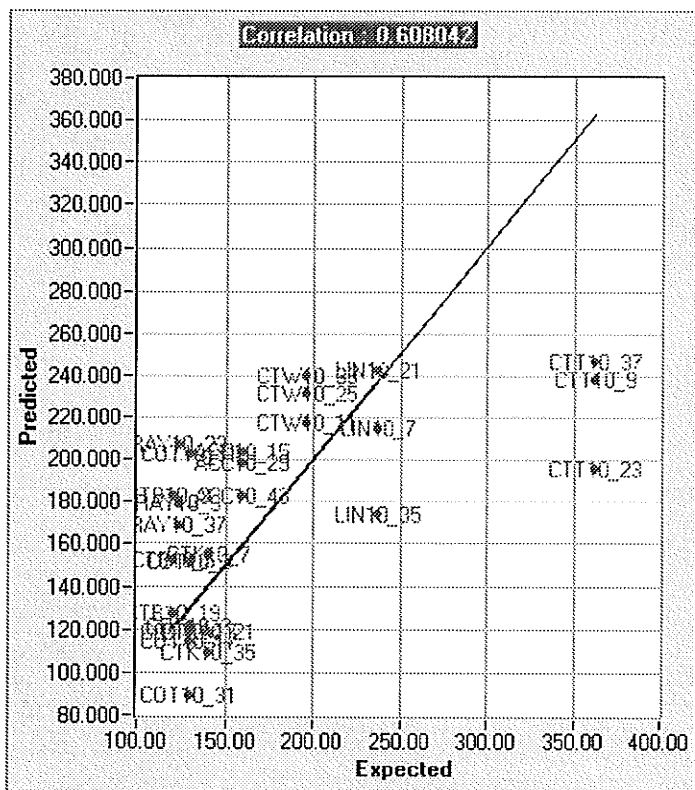


Figure 4.9 Linear regression (SSC) for Cellulose Fibres (all) vs Fabric weight

There were eight fabrics that were appropriate for this grouping, but there was a poor relationship between fabric weight and the sensor responses to the exposure to the same amount of odorant when all cellulose sources were included.

Cotton flannel
Cotton broadcloth
Cotton knit
Cotton terry cloth
Cotton twill
Linen suiting

Chemically and physically modified cellulose-based fibres:
Rayon (spun viscose challis)
Activated carbon cloth

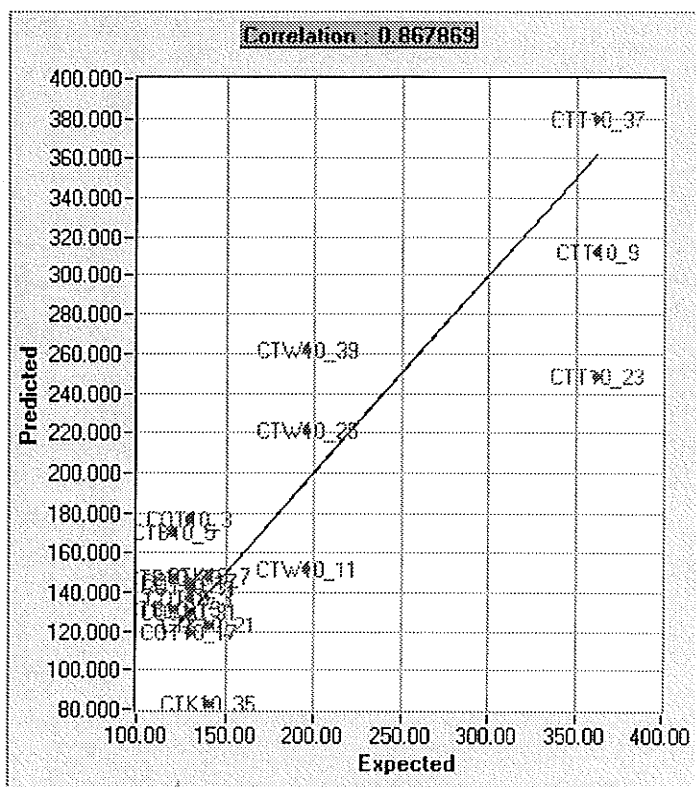


Figure 4.10 Linear regression (SSC) for All Cottons vs Fabric Weight

There were five fabrics that were appropriate for this grouping, but there was a very good relationship between fabric weight and the sensor responses to the exposure to the same amount of odorant when only the five cotton fabric sources were included.

- Cotton flannel
- Cotton broadcloth
- Cotton knit
- Cotton terry cloth
- Cotton twill

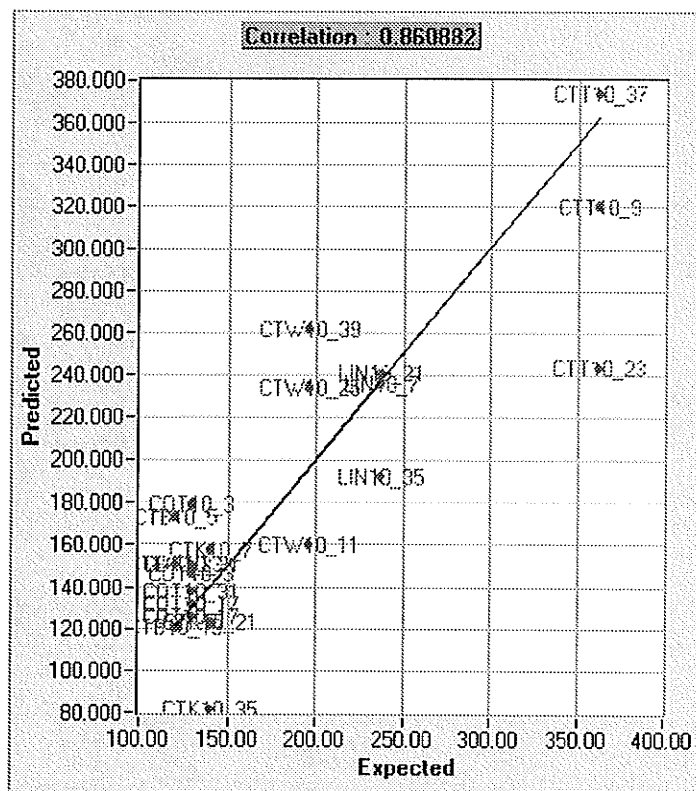


Figure 4.11 Linear regression (SSC) for Cellulose Fibres (cottons plus linen) vs Fabric weight

Six of the cellulose fibres, as above - with rayon and activated carbon cloth removed. In this case, the relationship is further improved.

All of the cotton fabrics are woven or knitted from unexposed cotton yarn.

Each of the two fabrics removed from the relationship have been processed from cellulose sources, but have been changed from the original. The rayon has been manufactured from cellulose sources such as wood pulp and cotton fibres that are too short for yarn manufacture. It is treated with alkali, then with carbon disulfide and then dissolved in sodium hydroxide - aged to become viscous enough to be extruded into fibre.

Activated carbon cloth is further manufactured from woven rayon cloth

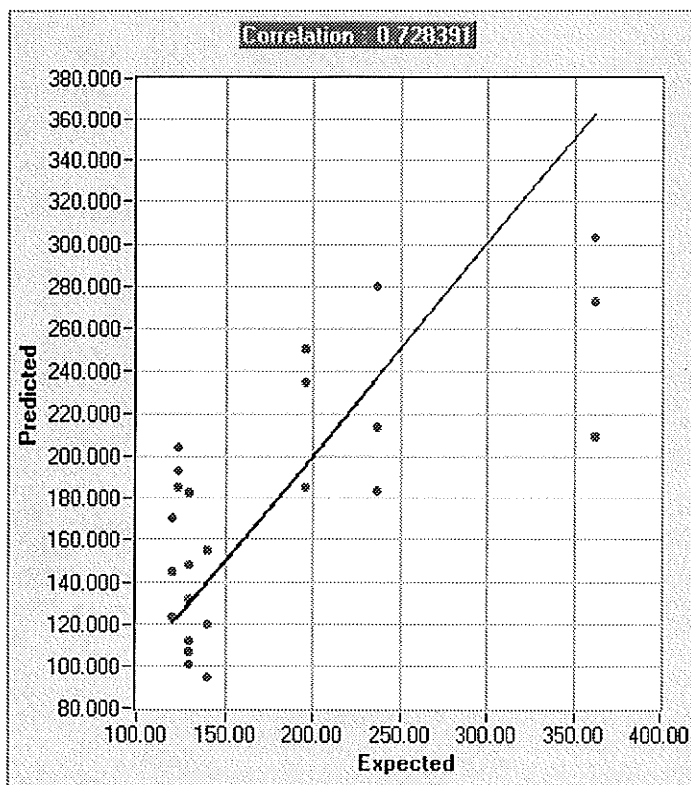


Figure 4.12 Linear regression (SSC) for Cottons plus LIN and RAY vs Fabric Weight

When all the cottons plus linen and rayon are included together, the correlation coefficient is reduced – presumably because the rayon being a processed cellulose rather than in its original state has changed sufficiently so that its adsorption properties no longer are common to this group.

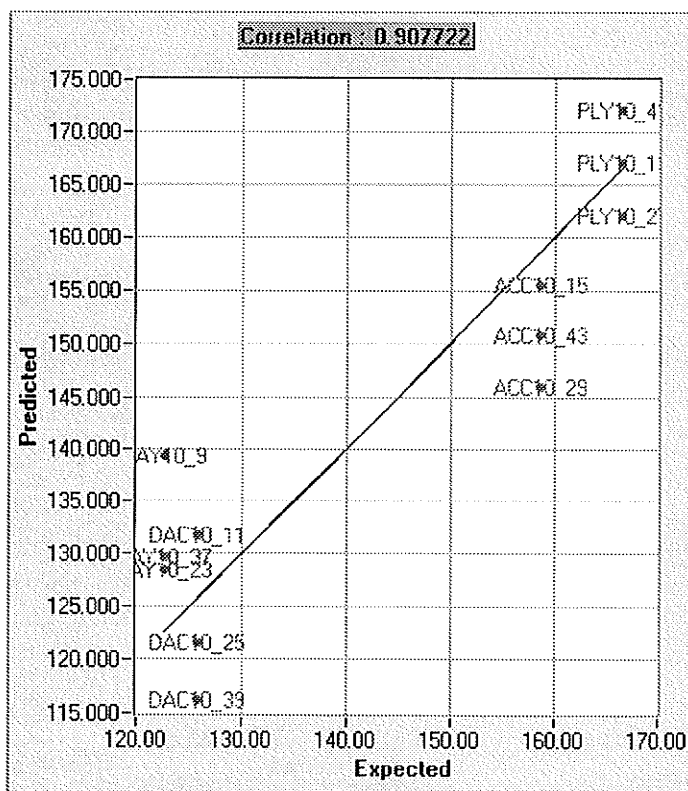


Figure 4.13 Linear regression (SSC) for Synthetic fibres - Fabric weight

Rayon
Spun polypropylene
Dacron type 54
Activated carbon cloth

Although there is no direct association between the nature of these fabrics, which have fibre sources that are very diverse, there is a high correlation between the signal and the fabric weight. This needs to be probed further, but may prove to be an artifact of other properties.

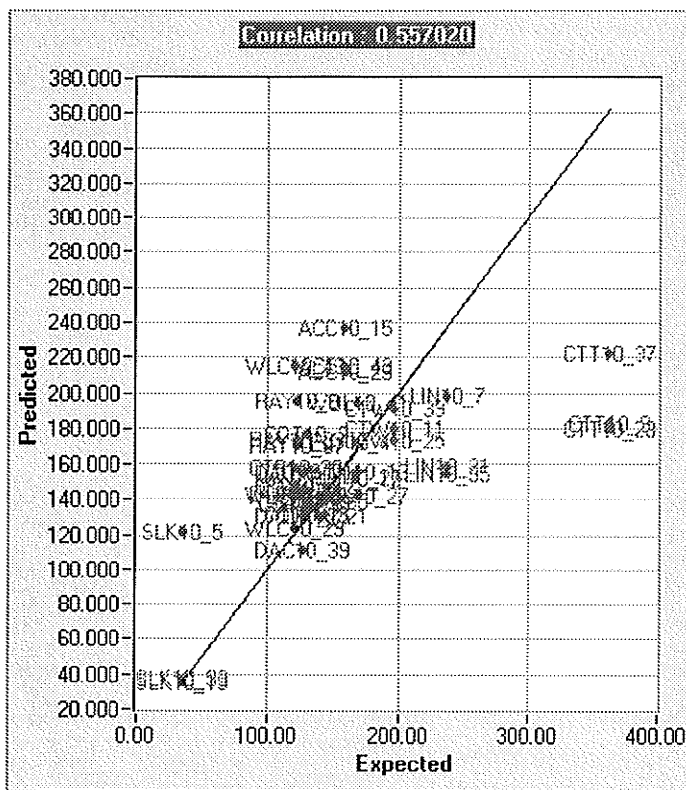


Figure 4.14 Linear regression (SSC) for all 13 Fabrics vs Fabric Weight

When all of the fabrics tested are combined, fabric weight is poorly correlated with sensor response

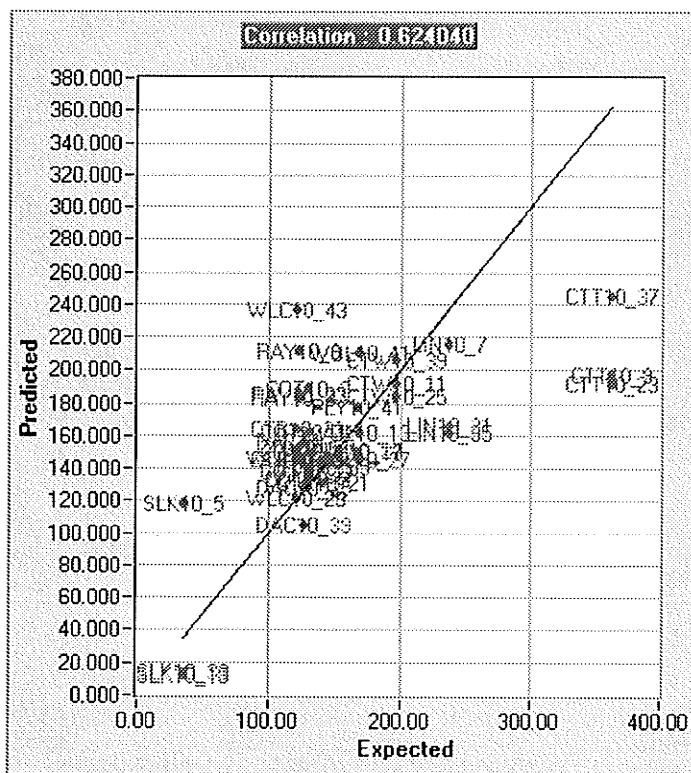


Figure 4.15 Linear regression (SSC) for All Fabrics minus ACC vs Fabric Weight

As for Figure 4.19, the removal of ACC from the mix of fabrics in this analysis improves the correlation only slightly.

4.3.3.3.2 Graphs Relating Fabric Density and Sensor Signal Intensity

Density is the weight of fabric per unit volume of the fibres in the fabrics being tested.

Density is a constant which is characteristic of a particular fibre – so that all of the cottons would have the same density, as would the wools.

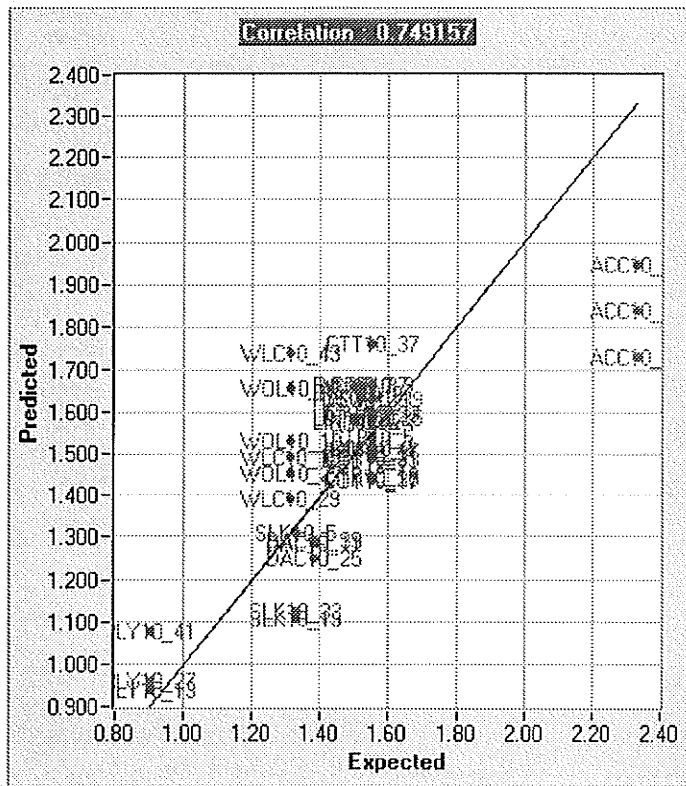


Figure 4.16 Linear regression (SSC) for All 13 Fabrics vs Density

The correlation between the density of the fibres that make up the fabrics did not appear to be highly related to the adsorption of odors as measured by the sensors.

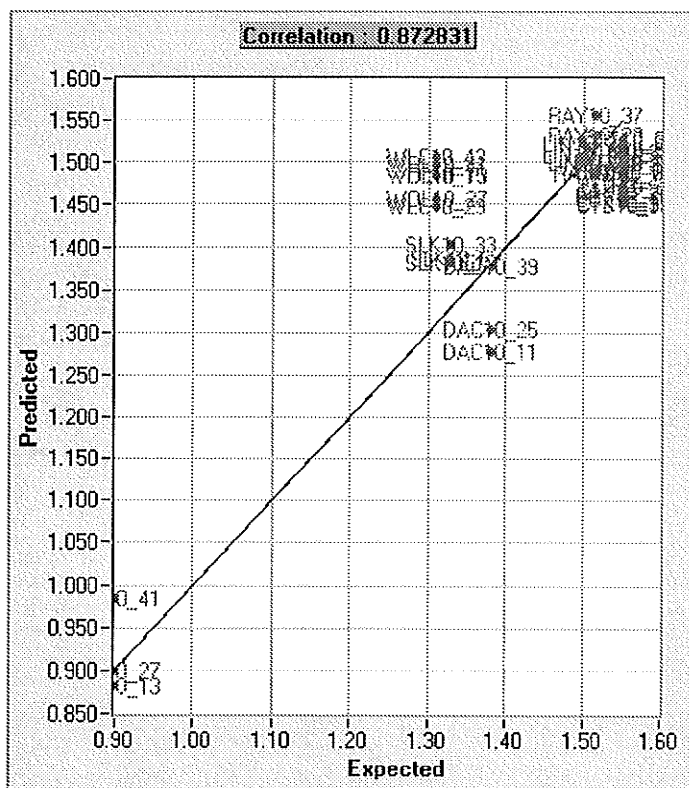


Figure 4.17 Linear regression (SSC) for Fabric Set with ACC removed (12 fabrics only) vs Density

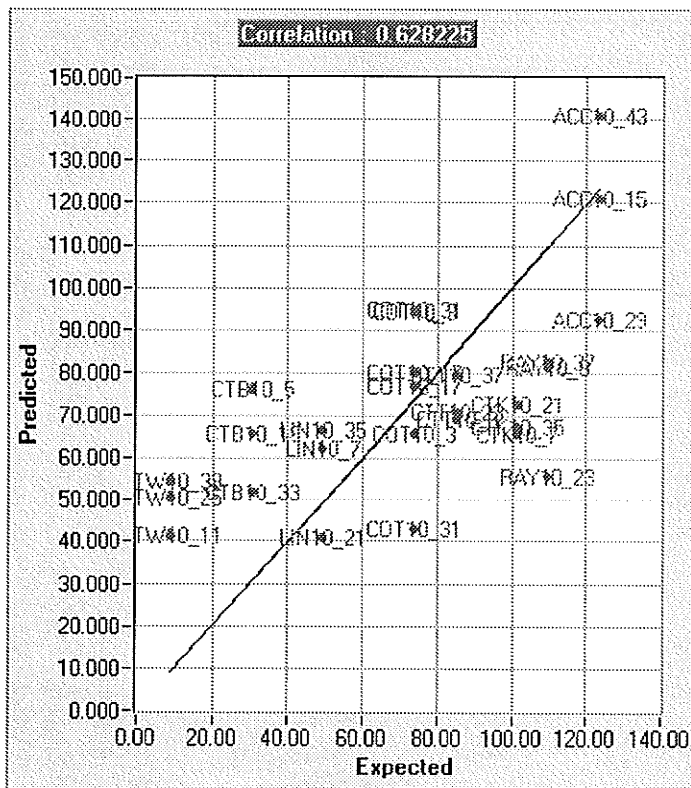
When activated carbon cloth (ACC) is removed, the correlation between the density of the fibres that make up the fabrics improved greatly. The treatment applied to the ACC appears to change it so that its attributes do not always behave in the same manner as untreated fibres in the other cloth forms.

Air permeability is the amount of air which can be passed through the fabric at a given pressure

Correlation: 0.857966

ID	Expected	Predicted
#0_27	58.0	75.0
#0_41	57.0	57.0
#0_13	57.0	55.0
SLK#0_5	82.0	68.0
SLK#0_33	81.0	81.0
SLK#0_19	83.0	84.0
WLC#0_29	95.0	93.0
WLC#0_15	95.0	86.0
WLC#0_43	95.0	95.0

There is a high correlation for the amount of air that can move through the fabric and the signal from the sensors.



Rayon (spun viscose challis)
Activated carbon cloth

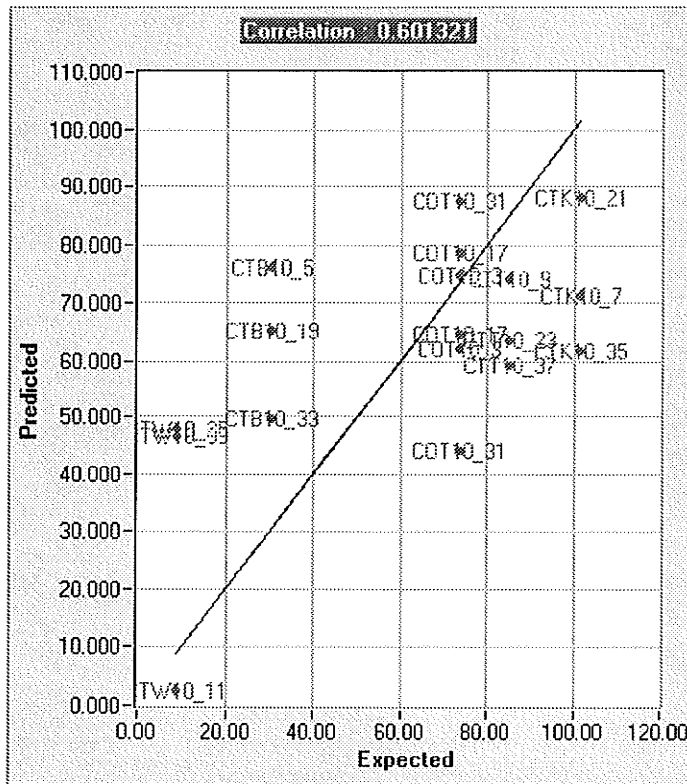


Figure 4.20 Linear regression (SSC) for Cotton Only vs Air Permeability

When only the 5 cotton fabrics were used there was poor correlation between air permeability and the sensor responses.

- Cotton flannel
- Cotton broadcloth
- Cotton knit
- Cotton terry cloth
- Cotton twill

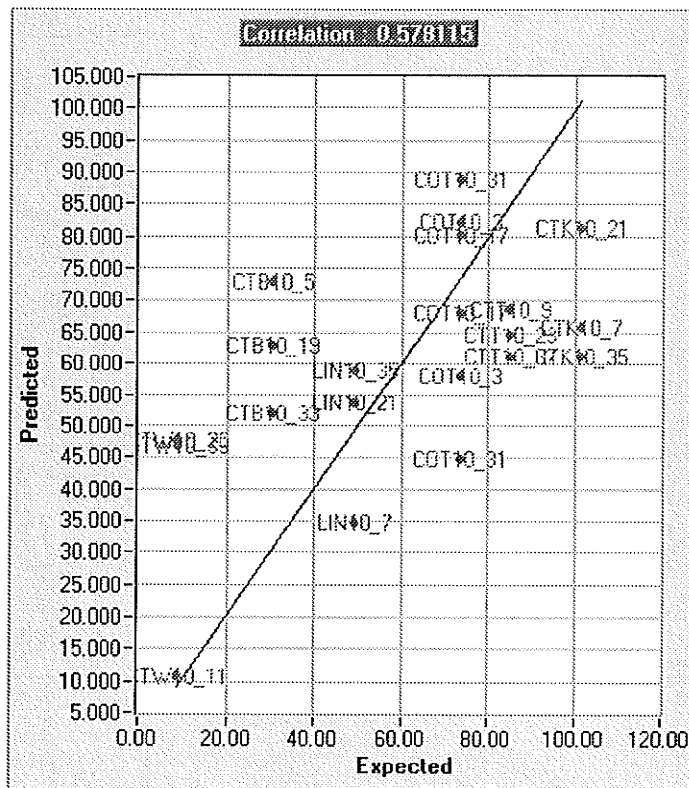


Figure 4.21 Linear regression (SSC) for Cellulose fibres (Cottons plus LIN) vs Air permeability

When both Activated carbon cloth and rayon removed from the analysis of all of the cellulose fabrics, there was poor correlation between air permeability and the sensor response for the remaining cotton and linen fabrics.

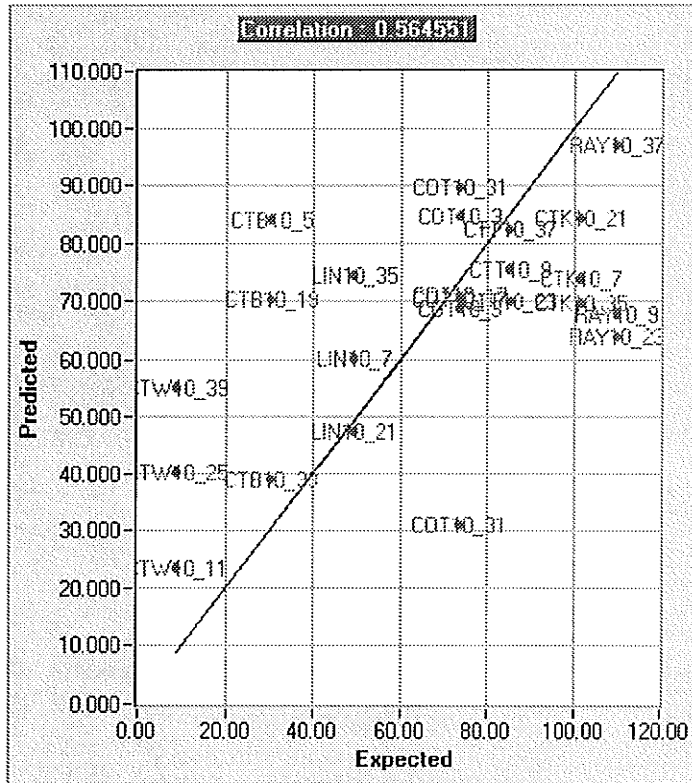


Figure 4.22 Linear regression (SSC) for Cellulose fibres (minus ACC) vs Air permeability

Activated carbon cloth removed from the analysis. There is poor correlation between air permeability and the sensor response.

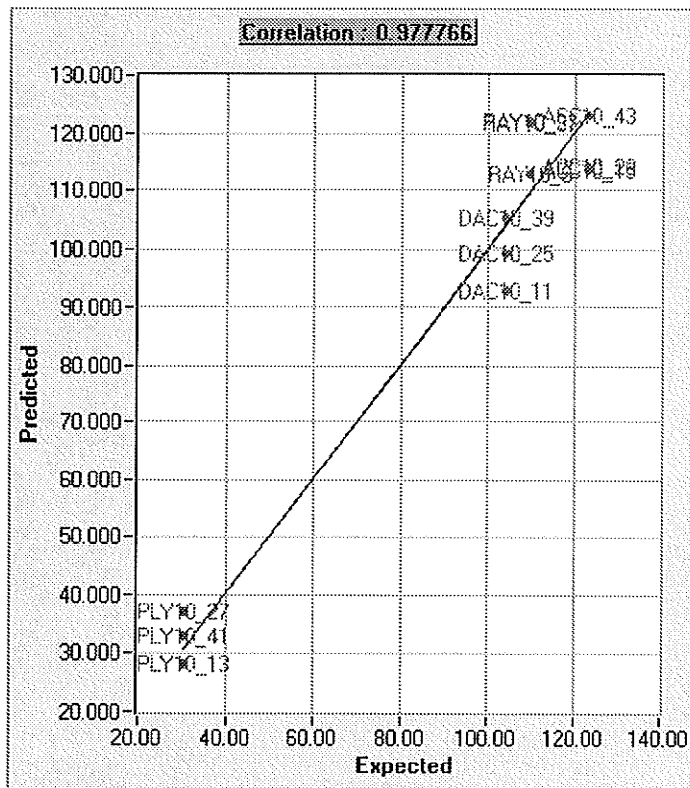


Figure 4.23 Linear regression (SSC) for Synthetic Fibres vs Air permeability

There is a very high correlation for the various synthetic fabrics included here with the amount of air that can pass through the fabrics and the sensor signals for odorant presence.

4.3.3.3.4 Graphs Relating Fabric Porosity and Sensor Signal Intensity

Porosity is a measurement of the % air contained in the fabric, both within the woven or knitted structure and within the yarns that form the fabric. This could be associated with the amount of odorized air that is trapped by the sample during the exposure process.

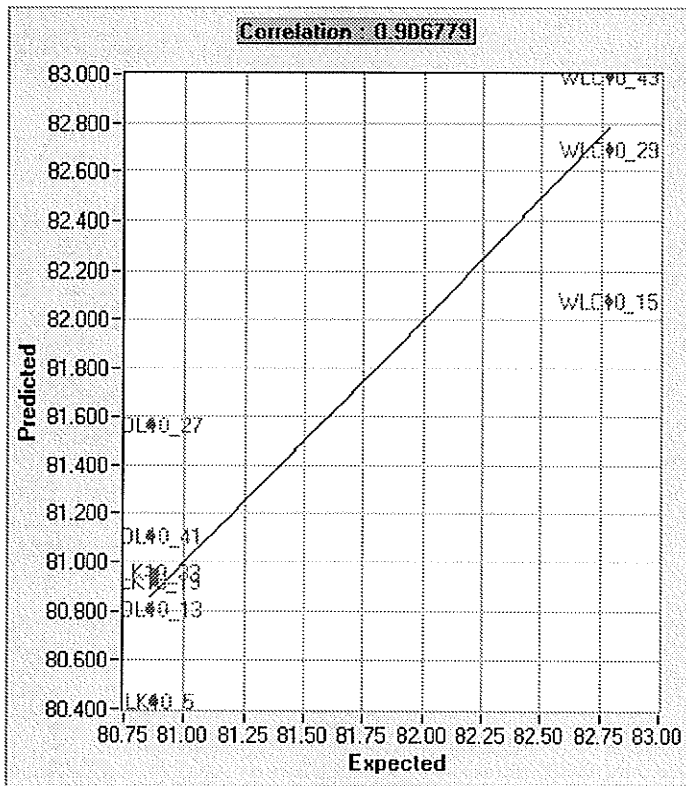


Figure 4.24. Linear regression (SSC) for Protein Fibres vs Porosity

Wool flannel
Wool challis
Silk

There is a high correlation for the amount of air that can be contained within the fabric and the signal from the sensors.

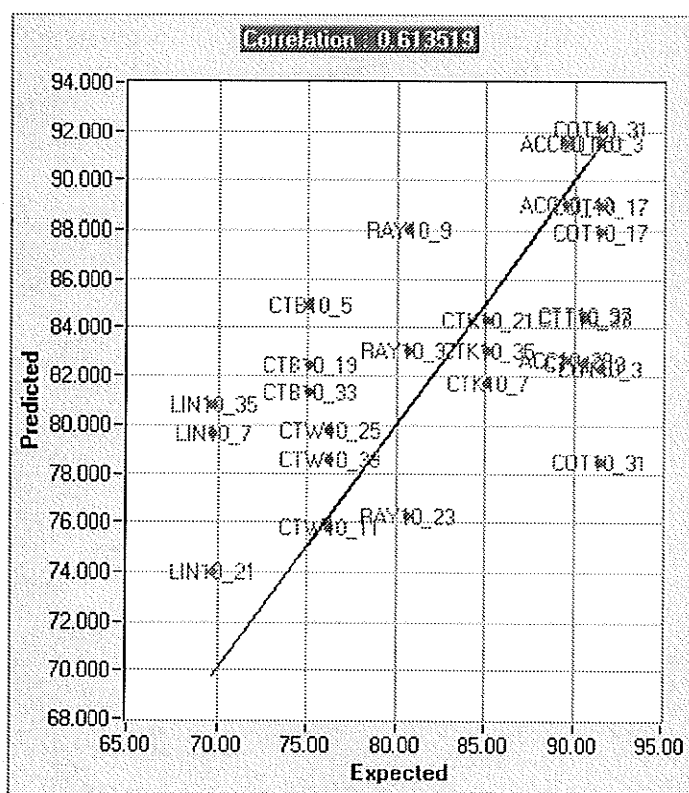


Figure 4.25 Linear regression (SSC) for Cellulose fibres (all) vs Porosity

All eight cellulose based fabrics are included and a fairly large range of values for porosity. There is poor relationship between porosity and sensor signal for this set of samples.

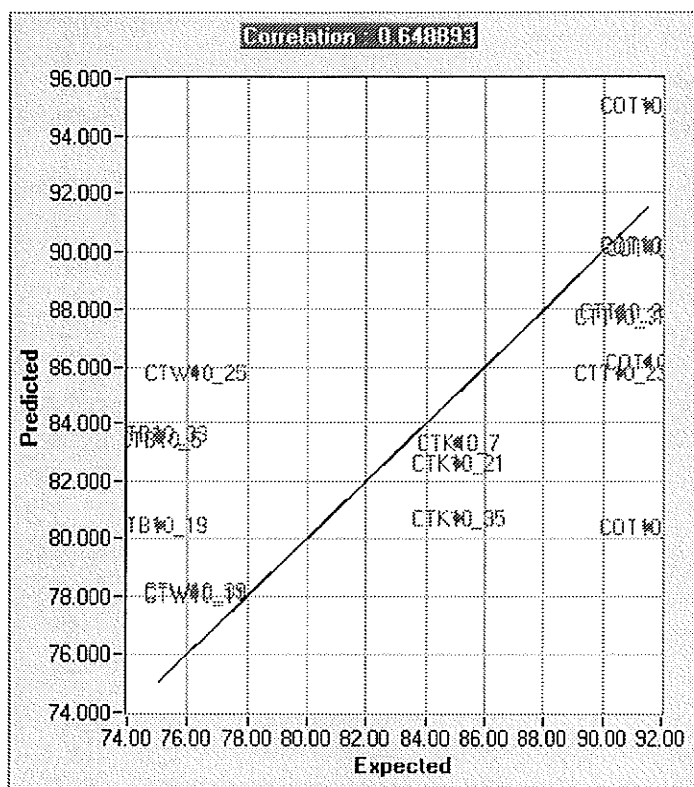


Figure 4.26 Linear regression (SSC) for Cottons Only vs Porosity

When only the 5 cotton fabrics were used there was poor correlation between porosity and the sensor responses.

- Cotton flannel
- Cotton broadcloth
- Cotton knit
- Cotton terry cloth
- Cotton twill

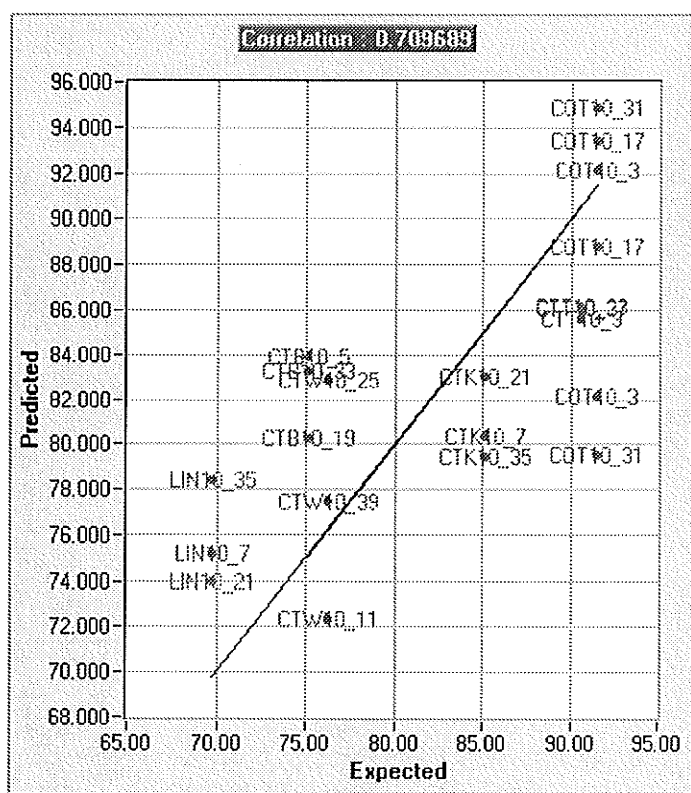


Figure 4.27 Linear regression (SSC) for Cottons plus Linen vs Porosity

When linen is added to the cotton fabrics in Figure 4.31, the correlation is improved but not greatly for the sensor signals vs porosity for these samples.

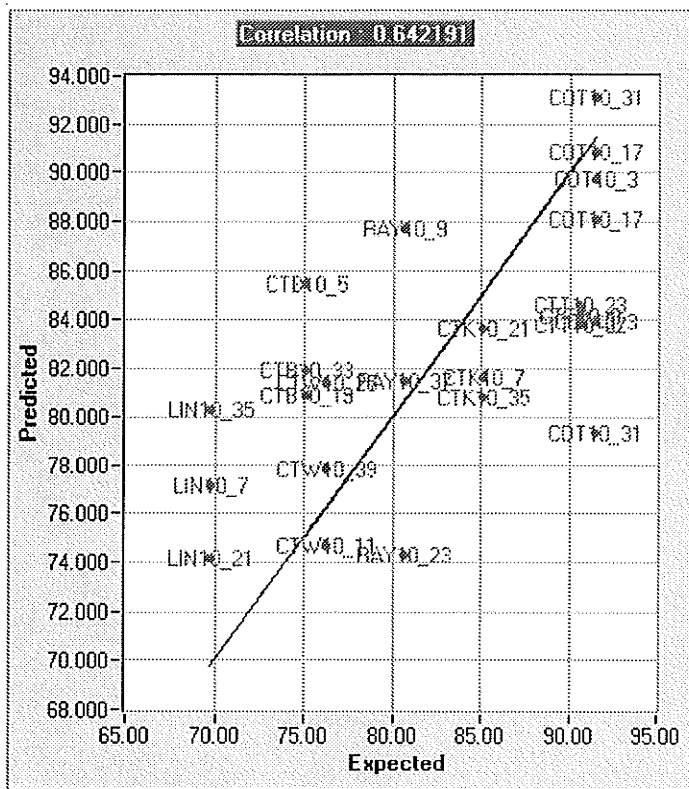


Figure 4.28 Linear regression (SSC) for all Cellulose fibres (minus ACC) vs Porosity

The correlation coefficient relating the sensor signals from all of the cellulose fabric samples, except ACC, to the values for porosity for each of the fabrics was poor.

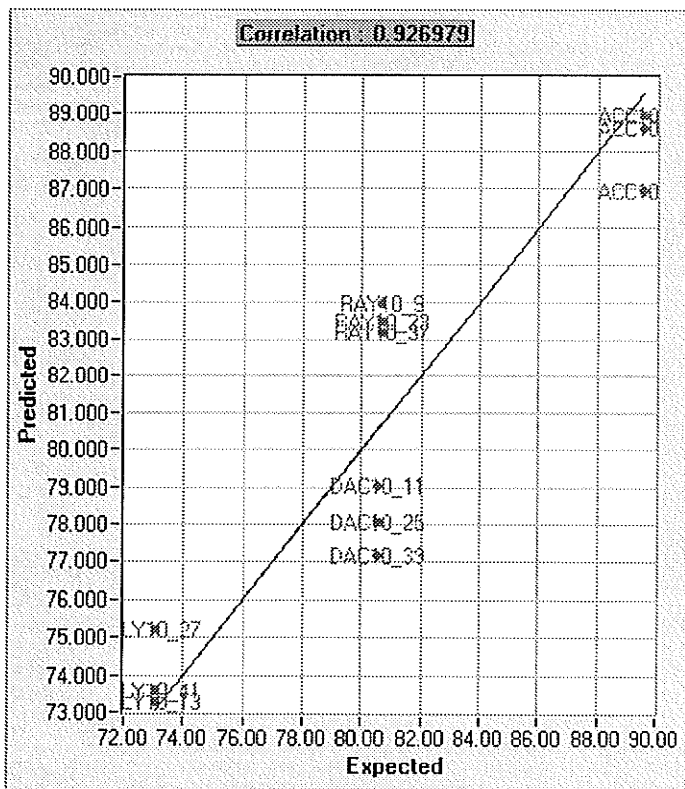


Figure 4.29 Linear regression (SSC) for the Synthetic fibres vs Porosity

The fabrics included here are:

- Activated carbon cloth
- Rayon
- Dacron type 54
- Spun polypropylene

Although there is no direct association between the nature of these fabrics - having fibre sources that are very diverse - there is a very high correlation between the signal and the porosity. This needs to be probed further.

4.3.3.3.5 Graphs Relating Fabric Thickness and Sensor Signal Intensity

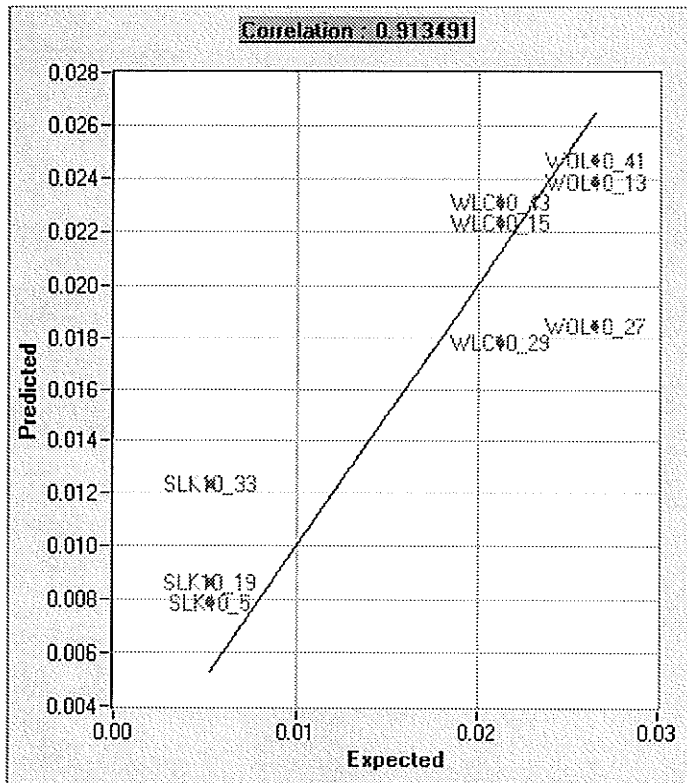


Figure 4.30 Linear regression (SSC) for Protein Fibres vs Thickness

There is a high correlation for the relationship of the sensor signals to the fabric thickness.

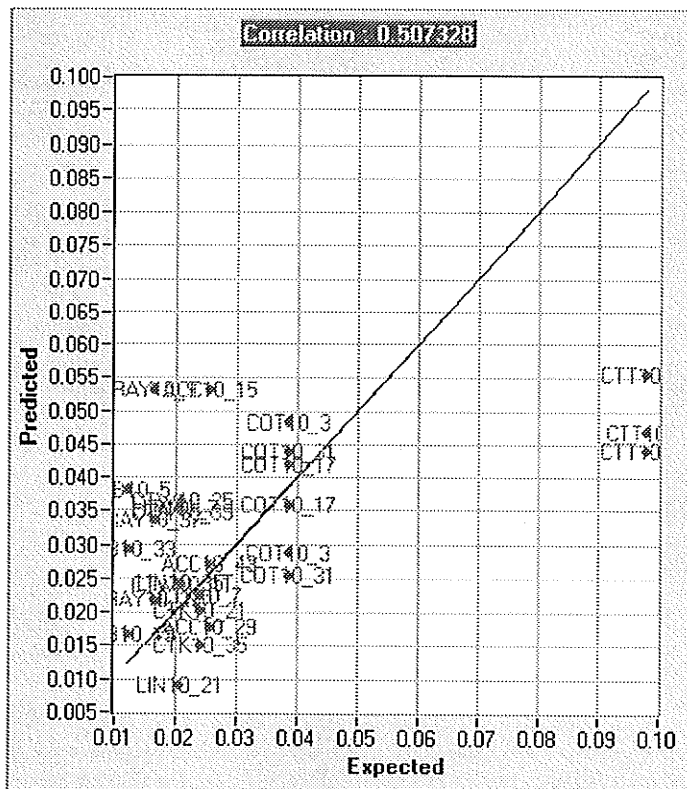


Figure 4.31 Linear regression (SSC) for All Cellulose Fabrics vs Thickness

When all eight cellulose fabrics were used there poor correlation between fabric thickness and the sensor responses.

Cotton flannel .
Cotton broadcloth
Cotton knit
Cotton terry cloth
Cotton twill

Plus
Linen
Rayon
Activated carbon cloth

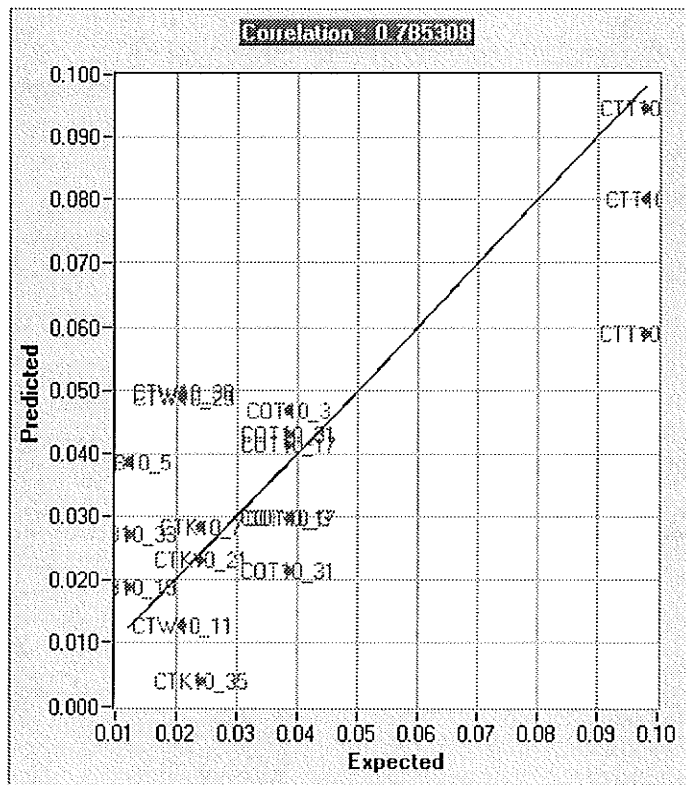


Figure 4.32 Linear regression (SSC) for Cottons Only vs Thickness

When only the 5 cotton fabrics are included, the correlation between the sensor readings and the fabric thickness was moderately good.

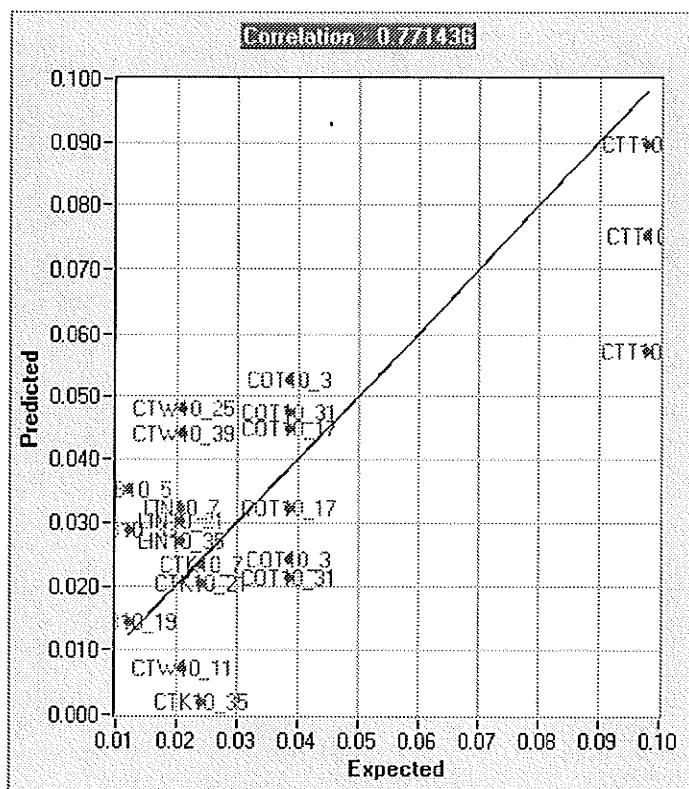


Figure 4.33 Linear regression (SSC) for Cottons plus Linen vs Thickness

When linen was added to the five cotton fabrics, the correlation between the sensor readings and the fabric thickness was not changed appreciably.

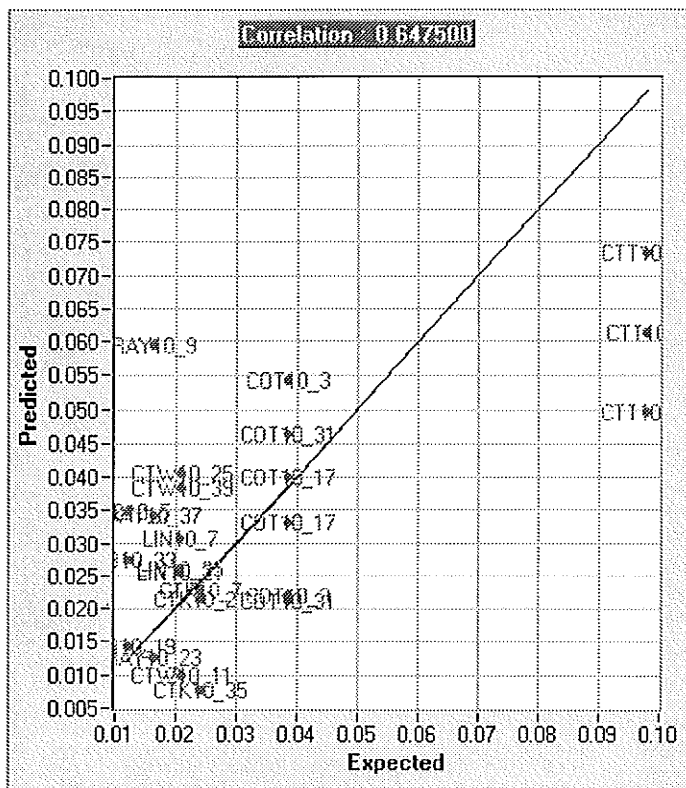


Figure 4.34 Linear regression (SSC) for All Cellulose Fabrics vs Thickness

The correlation coefficient for all of the cellulose fabrics (cottons, linen plus rayon) with fabric thickness was poorer than when rayon was not included.

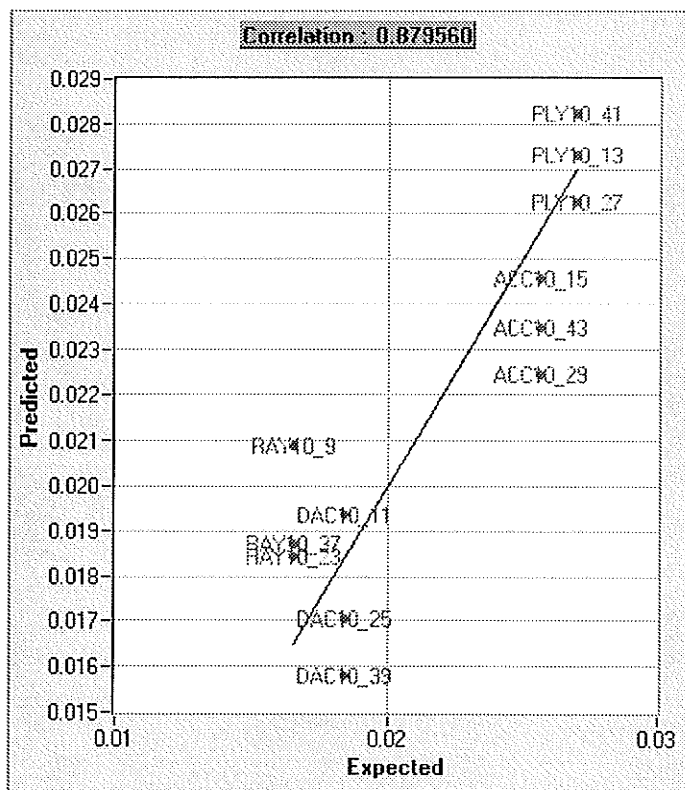


Figure 4.35 Linear regression (SSC) for All Synthetic Fabrics vs Thickness

The correlation between the synthetic fabric thickness and the sensor readings was good.

4.4 Discussion and Conclusions

The purpose of this study was to establish the various components necessary to develop a standard test system for environmental testing of malodors. Several relationships were established in the first part of the study.

1. The exposure system and swine odor simulant were successfully used to create samples for sensory and electronic nose analysis in the Alpha MOS Fox 3000. Using these components, it was possible to establish the initial test conditions and protocols that allow stabilization of odors onto cloth swatches for measurement.
2. All of the cloth sources tested were able to retain the swine odor simulant components to a level that could be perceived by the human sense of smell. Cloth types could be identified from these results as more or less likely to be useful, so that the fabrics for further work could be chosen from the group of best performing fabrics. While activated carbon cloth did not perform well in sensory analysis, the adsorbed swine odors were released during electronic nose analysis. The nature of this fabric, which was designed to adsorb and retain odors, placed it in the group of fabrics that would be explored in further testing.
3. The samples were stable to analysis over the period of time of the sensory studies, i.e., for the same day preparation and four uses during testing.
4. Both methods of sensory data collection were effective in evaluating the differences between the exposed and unexposed samples for odor uptake. Statistical analyses demonstrated these differences to be significant in all fabrics for both methods. Informal questioning for panelists' preferences for each of the scaling methods showed no clear preference for either method. All found both methods straightforward and easy to accomplish.
5. Appropriate test conditions were established for electronic nose analysis of odors stabilized onto fabrics. The Alpha MOS Fox 3000 electronic nose data were successful in demonstrating the differences in exposed and unexposed samples. Therefore, it was an appropriate tool for the measurement of the presence of malodor in air samples. It would be

used to explore further the relationship between the sensory responses and the e-nose responses. The electronic nose was also able to distinguish among the fabrics used in the study before exposed to swine odor simulant.

In the second analysis of the data, the differences among the fabrics for odor uptake following SOS-exposure were evaluated using analysis of variance and multiple comparison testing. The results showed the following relationships.

6. The groupings from REGWF multiple comparisons were not very clear, as there was much overlapping of groups and mixing of the different fibre types. There were clear groupings for the lower mean scores for linen, cotton terry cloth, and activated carbon cloth and these three fabrics would be eliminated from use in sensory testing. However, activated carbon cloth could still be of interest for use in testing with an electronic nose. It was designed to adsorb and retain odors, and would release the odors when heated, and so it held potential for electronic nose analysis of environmental malodors.
7. The fabrics that both adsorbed and released odor to give the highest sensory means did not form a neat pattern based on fibre type or surface chemistry, but were distributed throughout both. The fabric that performed best for this was cotton knit (a cotton single knit), which was very difficult to manipulate due to its tendency to curl from its knit structure.

In the third part of this study, the measured physical attributes of the fabrics were compared to the sensory scores and to the sensor readings.

8. Multiple regression formulas were calculated for predicting sensory scores using the physical attributes of the fabric types. The R^2 values for the test within the cotton group was much higher than the relationship across all fabrics.

All fabrics included:

$$\text{LMS (log value)} = 1.7823 - 0.0012 (\text{FW}) - 0.4569 (\text{D}) + 0.0009 (\text{AP}) \text{ adjusted } R^2 = 0.4651).$$

$$\text{DFC} = 108.2146 - 0.0962 (\text{FW}) - 29.6684 (\text{D}) - 0.0429 (\text{AP}) \text{ (adjusted } R^2 = 0.6694).$$

The five cotton fabrics only:

$$\text{LMS (as log value)} = 1.2408 - 0.0019 (\text{FW}) + 0.0022 (\text{AP}) \text{ (adjusted } R^2 = 0.9924).$$

$$\text{DFC} = 66.06803 - 0.1263 (\text{FW}) + 0.0575 (\text{AP}) \text{ (adjusted } R^2 = 0.8375).$$

Where FW = fabric weight in g/m^2

D = density in g/cm^3

AP = air permeability in cc/cm^2

LMS = predicted value for odor intensity on labelled magnitude scale (as a log value)

DFC = predicted value for odor intensity on difference-from-control scale

From this, higher sensory scores for the same treatment were associated with lower fabric weight and density and higher air permeability when all fabrics were included. When only cotton fabrics were used, density was a constant, and higher sensory scores for the same treatment were associated with lower fabric weight and higher air permeability.

9. The electronic nose data were examined for relationships between the sensor readings for the exposed swatches and the physical attributes measured for the fabrics. The sensor readings were most highly correlated for the synthetic and the protein fibers with fabric weight, air permeability, porosity and thickness. Correlation coefficients were not as high for cotton samples and for cotton plus linen samples for fabric weight and thickness, and were poorer for all other relationships. Fabric density, which was a constant for each fiber, was somewhat correlated with the sensor signals for the exposed fabrics.

Chapter 5

Study #3: Evaluation of the Headspace Composition of Odors from Cloth Swatch Samples

5.1 Introduction

The principle of cloth swatch sampling of environmental malodors was that the components of the odor that were important in its assessment would be adsorbed onto the cloth surface which would release these odors when the swatch was evaluated. Understanding the stimulus was a challenge because an environmental malodor was not usually made up of only one culprit-compound. Rather there were generally a large number of possible compounds, sometimes hundreds, depending on the source of the malodor. This complexity was accompanied by potential odor synergies, masking and enhancement phenomena in the stimulus, and potential various odor blindnesses and specific anosmias in those perceiving the odors.

This was the first of three studies planned to examine aspects of the cloth swatches that were identified in Study #2 as potentially useful for environmental odor sampling applications. The purpose of this small study was to evaluate the interaction between the cloth swatches and the mixture of chemicals that simulates much of the sensory identity of swine odor used to test the fabrics in Study #2. While both sensory and electronic nose testing had given a picture of which fabrics might be the most useful in conducting actual environmental tests, there was no direct information on what is actually happening in the uptake and release of the odors from the fabric swatches. This aim of this work was to clarify the composition of the headspace in the sample containers, as the headspace formed the volatile sample that both the sensory assessors and the electronic nose evaluate. This work was undertaken without specific funding allocated and as such required access to other groups who would be able to cooperate in the work.

The first approach was a GC/MS analysis of the headspace in the swatch samples. Two types of sampling systems were used for the GCs, dynamic and static. The dynamic system used a vacuum in the sampling process and basically pulled everything off the sample, which in this case would remove the adsorbed odor from the cloth swatches as well as the head. The static system

samples the headspace in a manner which would simulate the situation for the sensory panels and for the auto-sampler of the electronic nose where the sampling in both cases was “sniffing”.

Wampler (2002) discussed the use of static sampling methods and stated that when a given sample (in this case specifically a food stuff) was placed in a confined sampling container and the concentration of a compound reached about 1 ppm in the headspace, it could be taken as a simple injection of an aliquot of the atmosphere in the vessel.

Another approach was possible as well through electronic nose analysis, and would be used to compare to the GC/MS analysis. It was possible to use the Alpha MOS AlphaSoft Version 8 software for principal component analysis to manipulate the data and remove partial components of signals (Bredzinski, 2004, personal communication). This concept would be used to remove the cloth component from the corresponding cloth plus swine odor simulant signal to create the headspace odorant signal alone. The same could be done with samples of the individual components of the swine odor simulant, which had been sampled onto cotton flannel. This allowed the headspace signals of the individual components to be compared to the headspace signals of the 13 cloth swatches exposed to the odor mixture to attempt to clarify which odorants were most likely present.

The hypothesis was that components of the swine odor simulant would be adsorbed onto the fabric surfaces and released to form the headspace odor in the cassettes or vials, and that these components could be identified through GC/MS and electronic nose analyses. The expected data would provide the relative proportions of each of the components of the swine odor simulant that were present in the headspace and would demonstrate what the swatches are capable of sampling from the mixture of compounds supplied to them in the exposure system.

5.1.1 Objectives and Hypotheses

The overall objective of this study was to evaluate the headspace sample available to the panelists and to the electronic nose. The fabrics adsorb, retain and release odor - but it was not clear which components were involved in forming the odor stimulus. There were two methods to

determine headspace composition. The first was GC/MS analysis for headspace composition of each of the samples. The second was data manipulation to isolate the sensor patterns for each of the fabric headspace samples independent of the base fabric used. From this, the sensor patterns could be compared to the swine odor simulant signal and the signals from each of the components.

Hypothesis I: that all components were adsorbed onto the surface of the fabrics, retained and released equally as shown by the percent composition of each headspace sample from GC/MS analysis.

Hypothesis II: that all components were adsorbed onto the surface of each of the fabrics, retained and released equally as shown by the mapping pattern for the residual signals in principal components analysis.

5.2 Methods and Materials

This study was planned to use the 13 fabrics from Study 2 to compare the headspace of the unexposed and exposed samples of each for their odorant composition. In this way it was hoped to establish which components were adsorbed and released from the cloth swatches and formed the actual odor sample that the sensory panel and the electronic nose evaluated. The GC/MS analysis was to be done through the Department of Chemistry, University of Manitoba.

5.2.1 Cloth Swatches

In preparation for GC/MS analysis, a set of preliminary samples of cotton flannel, spun polypropylene, Dacron type 54, and activated carbon cloth were each treated with the swine odor simulant at the operating level for this study (2L/min for 5 min using the swine odor simulant from Chapter 4). The composition of the swine odor simulant is given in Table 5.1. Ultimately, only the cotton flannel was used in the preliminary testing.

Table 5.1. Composition of Swine Odor Simulant used for testing cloth swatches.		
Electronic Nose Code	Component	Swine Odor Simulant ppm
ACE	acetic acid	1500
PRO	propanoic acid (propionic acid)	375
ISB	2-methyl propanoic acid (isobutyric acid)	600
BUT	butanoic acid (n-butyric acid)	250
ISV	3-methyl butanoic acid (isovaleric acid)	300
VAL	pentanoic acid (N-valeric acid)	100
PHE	phenol	25
CRE	4-methyl phenol (p-cresol)	75
IND	indole	7.5
SKA	3-methyl indole (skatole)	5
NH4	ammonium hydroxide (NH ₄ OH) 5%stock solution	adjust to pH 8.2

The cloth swatch samples prepared for electronic nose analysis were the same as those used in Study #2, (i.e., the 13 fabrics, unexposed and exposed). Another set of samples was prepared using cotton flannel and the individual components of the swine odor simulant at the concentration at which they are present in the mixture with and without pH adjustment. The fabrics are given in Table 5.2. A trial sample of treated cotton flannel washed with methylene chloride was also prepared.

Table 5.2. Fabrics selected for evaluation for odor uptake of odor components.	
Sample Code (EN)	Fabric Description
CTK	cotton - flannel, bleached
PLY	cotton broadcloth, bleached, mercerized, combed
SLK	cotton - knit - bleached cotton t-shirt fabric
DAC	cotton - 9.5 oz, bleached terry cloth
RAY	cotton - twill, bleached, mercerized
WOL	wool - worsted flannel
COT	wool challis
CTB	silk habutae 8 mm
CTW	linen - suiting
WLC	spun viscose challis (rayon)
LIN	Dacron type 54 (disperse dyeable)
CTT	spun polypropylene
ACC	activated carbon cloth

5.2.2 Chemical Analyses

Preliminary studies were conducted using a GC/MS with a static sampling system located in the Department of Chemistry at the University of Manitoba. The composition of the swine odor simulant was used to correlate with the composition of the headspace. The treated cloth swatch samples were evaluated using a Hewlett Packard 5890 A GC, with a 60 m DB5 column, and a VG Analytical 7070E (organic) mass spectrometer scanning from 30 to 260 molecular weights. Two initial trials were planned to provide guidance for the remainder of the work: Trial #1 used only the treated cotton flannel sample, headspace sample, and Trial #2 used the treated cotton flannel sample, washed with methylene chloride.

5.2.3 Electronic Nose Analyses

Electronic nose analyses were conducted using the test conditions established in Chapter 4. The test conditions for collection of electronic nose data were as follows:

incubation time: 15 min
incubation temperature: 40°C
acquisition time: 2 min
delay time (sensors restored to "zero" state): 18 min
carrier gas flow rate: 150 ml/min

All other standard conditions are as described in Chapter 4. The sample sets for swine odor simulant and components only were evaluated more than 2 weeks apart, so the data evaluated to determine whether adjustments were necessary due to potential sensor drift. The presence of drift was tested by mapping all samples from the two sets together, and examining the results for the untreated cotton flannel samples for the two sessions. This evaluation will show the degree to which the two sample sets map together in principal component analysis.

5.2.4 Data Analysis

Using the AlphaSoft Version 8.0 software, it was possible to remove the portion of the signal of the SOS-exposed swatches that was due to the cloth swatch itself. This process involves transferring the library file(s) into an Excel worksheet, subtracting the appropriate signals while maintaining the integrity of the library file format in Excel. Then the file was saved in the library format and could be used in its modified form with the multivariate analysis algorithms in AlphaSoft. (Bredzinski, 2004, personal communication).

Electronic nose data on each of the components at the concentration in the simulant were obtained. These were compared to the changes in the relative composition of the odors. All electronic nose data analysis was performed through AlphaSoft Version 8. The data were manipulated by transferring them to Microsoft Excel, performing the required steps and moving the data back into an AlphaSoft Version 8 library to be analyzed again.

The following steps were used for the data manipulations. Firstly, for each of the 13 cloth swatches, the odorant signal was calculated as

$$\text{signal}_{\text{exposed}} - \text{signal}_{\text{unexposed}} = \text{signal}_{\text{odorant mix.}}$$

Then the signal for the cloth was subtracted from the “cloth plus treatment”, which corresponds to that sample. In this case, the mean signal for each of the sensors for each of the cloth samples was subtracted from each of the signals for the treated swatches of the same cloth sample (e.g. the mean signal from COT00 was subtracted from each of the signals for COT10 and recorded as a new dCOT result). Finally the data were moved back into AlphaSoft library file for analysis through the multivariate analysis algorithms available in this program.

The sample sets of exposed cloth swatches that were evaluated were, (1) the 13 fabrics – unexposed and exposed to the swine odor simulant and (2) cotton flannel plus each of the components alone, at the concentration that it is present in the SOS with the pH adjusted.

5.3 Results and Discussion

5.3.1 GC/MS Analysis of the Headspace Samples

The first sample analyzed was treated cotton flannel that was prepared for GC/MS analysis by injecting 0.75 ml of the headspace into the chamber. After 25 min of scanning there was no response, indicating that the concentration of the components present in the headspace was too low to be detected by the system. Two possible reasons were presented as to why the initial objective would not be feasible with the available equipment:

1. The concentrations were too low to be detected by the GC/MS in the headspace.
2. The components of the solution couldn't be evaluated as they had been changed by the presence of the ammonium hydroxide, which was a component of the swine odor simulant and was used for pH adjustment (Table 4.1).

Then the sample was analyzed with washing with methylene chloride, but this did not produce results. The conclusion of the analyst was that our samples were not of a sufficiently high concentration to be analyzed in the available equipment and further analysis would not be useful at this time (Buchanan, W., 2004, personal communication). These results prevented the testing of Hypothesis I. Future work would be in order to establish which components are present on the cloth itself and in the headspace through a dynamic sampling procedure and which components are present in the headspace (through a static sampling procedure). Another approach, which could be taken, was SPME sampling for analysis of the headspace. A third approach was through headspace mass spectrometry, which was available as another analysis method with additional equipment that could be added to the AlphaMOS Fox electronic nose systems. These systems work on the principle that the volatile components of a headspace were injected into the ionization chamber of a mass spectrometer without the separation step. A "fingerprint" was generated by the "simultaneous ionization and fragmentation of the mixture of molecules" that is characteristic of the particular sample (Alpha MOS, 2004, personal communication). The spectral information, which has been generated, allows the determination

of the sample composition (Pérès et al., 2003). Each approach required a larger scale funded project to accomplish.

5.3.2 Electronic Nose Analysis

While the components of a mixture that represent swine odor can be prepared analytically, it was not possible to predict from available chemical methods which odors would dominate in a mixture. All odorants present might or might not be “equal” in causing or contributing to the character or identity of the combination. This study would, however, attempt to demonstrate which signals were present in the sample headspace. The results of the electronic nose analysis of the cloth swatches and odor components are given in Figures 5.1 to 5.9.

Figure 5.1 shows mapping of the components of the swine odor simulant stabilized on cotton flannel compared to exposed cotton flannel. Components mapping close to the treated cloth were assumed to be adsorbed onto the cloth to form the odor present. In the map in Figure 5.1, there are three individual compounds and two groupings when the odorants are compared on cotton flannel, with the NH_4 and skatole mapping closer to the cloth than the other components. The results from Persaud et al. (1996) showed that indole, skatole and ammonia appeared to be the components most associated with the patterns from the swine odor. In this map, there were two groupings of the different acids and aromatics plus an individual position for acetic acid. In this case, indole mapped with the butyric, propanoic, and iso-butyric acids rather than closer to the treated cloth. This pattern continued in the other maps generated.

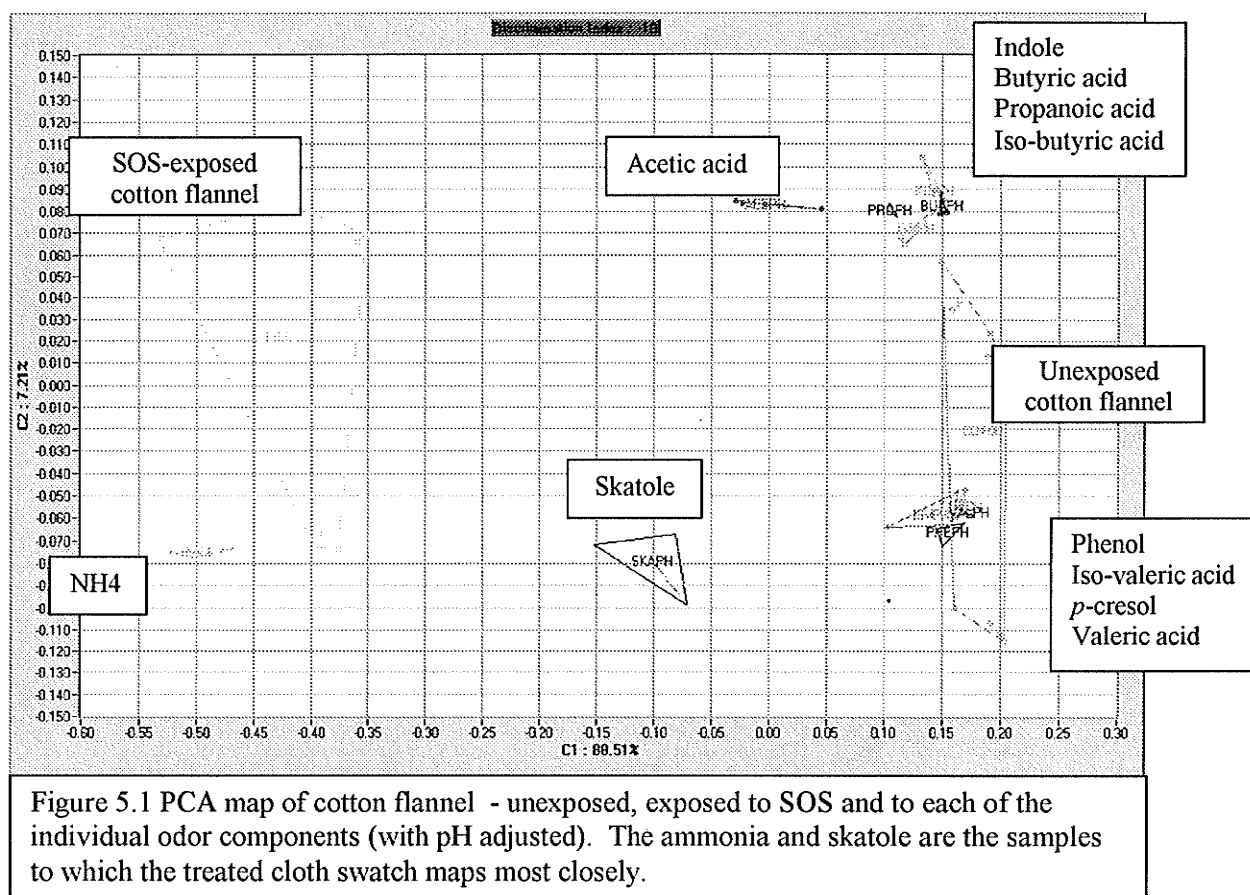


Figure 5.2 shows two maps – the upper one with all 13 exposed fabrics swatches and the lower one with the residual signals of each fabric once the unexposed fabric signal for that sample was removed. The upper map showed a large grouping from which only the spun polypropylene (PLY), silk (SLK), and Dacron (DAC) samples were completely separated, while the activated carbon cloth (ACC) mapped partly with the rest of the group. In the lower map the residuals from the activated carbon cloth and spun polypropylene samples were separate, while the silk and Dacron samples had mapped together away from the main group and also from the cotton knit (CTK) samples. There appeared to be very different combinations of components being adsorbed and released by the fabrics. The two most interesting parts of these maps were the positions of the spun polypropylene and activated carbon cloth samples. In the cloth form, the activated carbon cloth mapped more closely to the main group of cloth swatches, while as a residual signal, it was different from the other samples. The spun polypropylene always stood away from the group as well. Activated carbon cloth was produced for the purpose of odor adsorption and retention; so, future analysis on the nature of the compounds being released will be enlightening.

Figures 5.3 to 5.6 show the PCA maps of the relationships of the odor residuals for the different types of cloth used relative to the residuals from the individual SOS components. In Figure 5.3, all of the cotton samples were shown together, as the individual maps of the fabrics all showed the same patterns and relationships. Again the NH_4 , skatole and acetic acid were separate from the rest of the components and were mapped closer to the swatches indicating their importance in the residual odor.

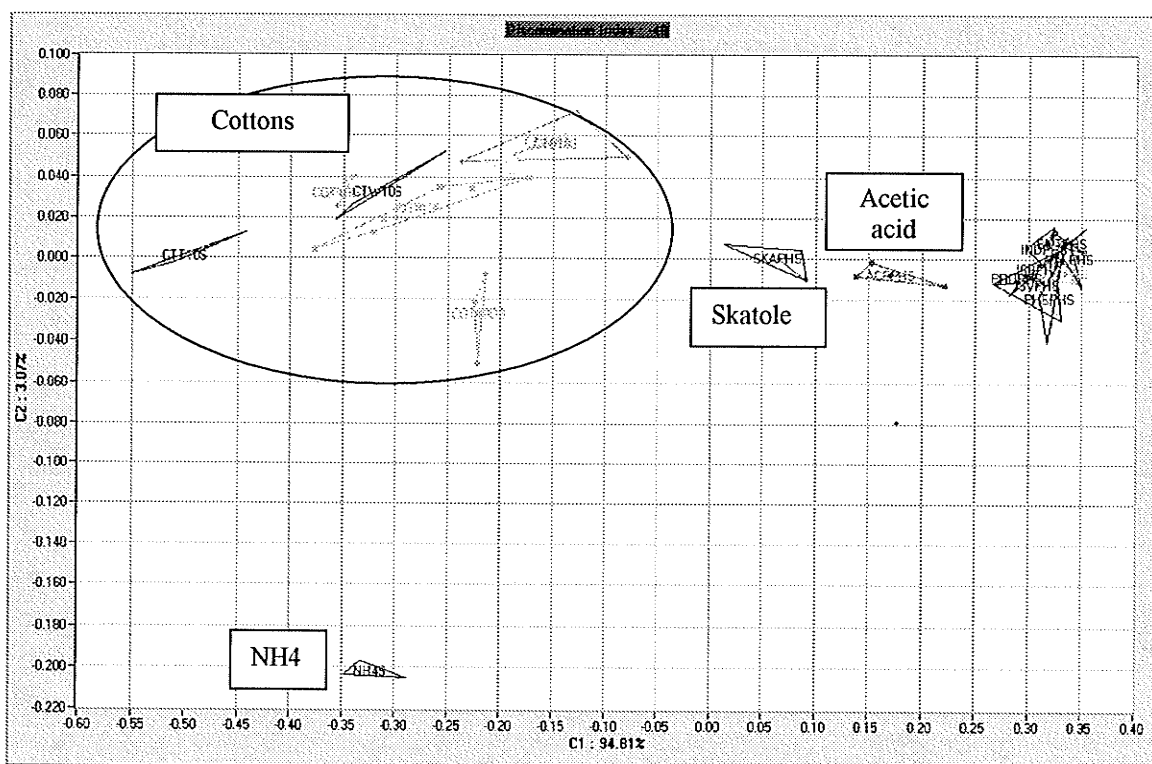


Figure 5.3. PCA map of the cotton sample residuals relative to the residuals from the SOS components. The 5 different cottons plus the 4 sets of readings on the cotton flannel standards are included.

Figures 5.4 and 5.5 show the principal component analysis maps for the residuals of the protein fibres and for linen, each with the residuals of the individual components. The same pattern was present as for the cottons in Figure 5.3. A different pattern emerged for one of the fabrics in Figure 5.6, the PCA map of the residuals of the three synthetic fibres – rayon, Dacron type 54, and spun polypropylene – along with the residuals for the individual components. In this case, the spun polypropylene sample residual mapped with the residuals of all of the components except NH_4 . In Study #2, spun polypropylene showed one of the best performances in retaining a stronger odor than did some of the other fabrics.

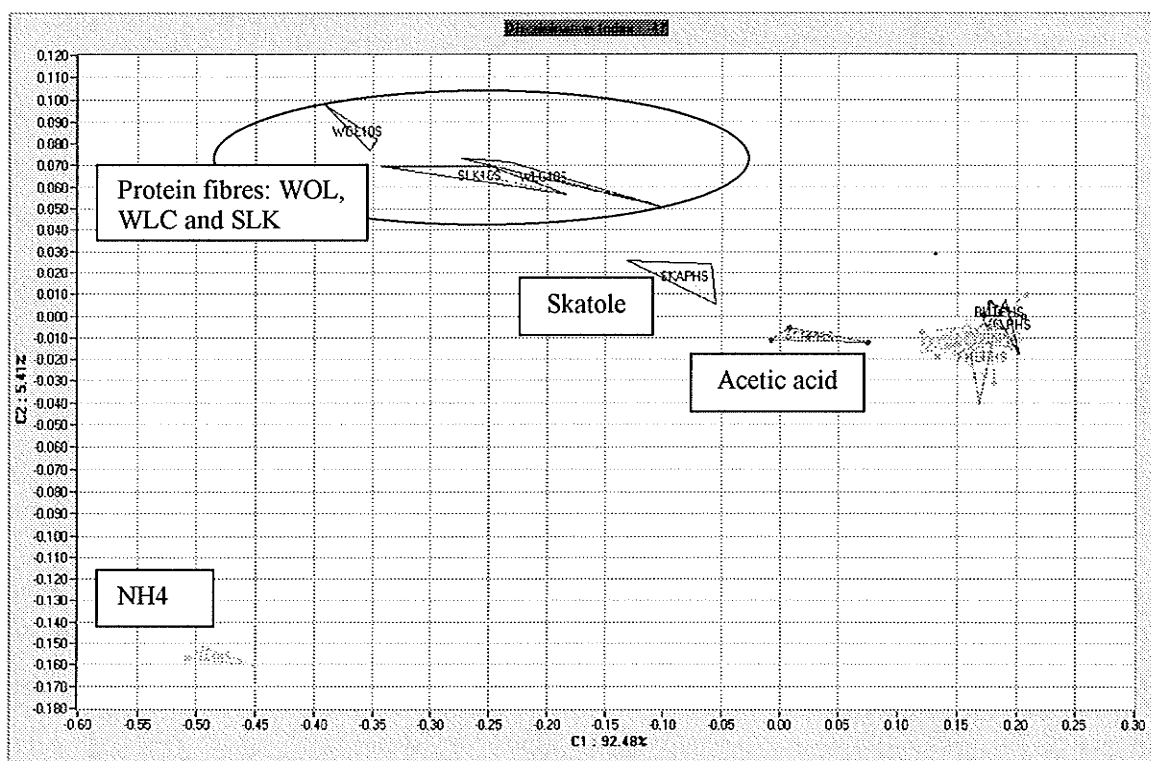


Figure 5.4. PCA map of all of the residuals of the 3 protein fibres (WOL, WLC and SLK) vs residuals of the individual components.

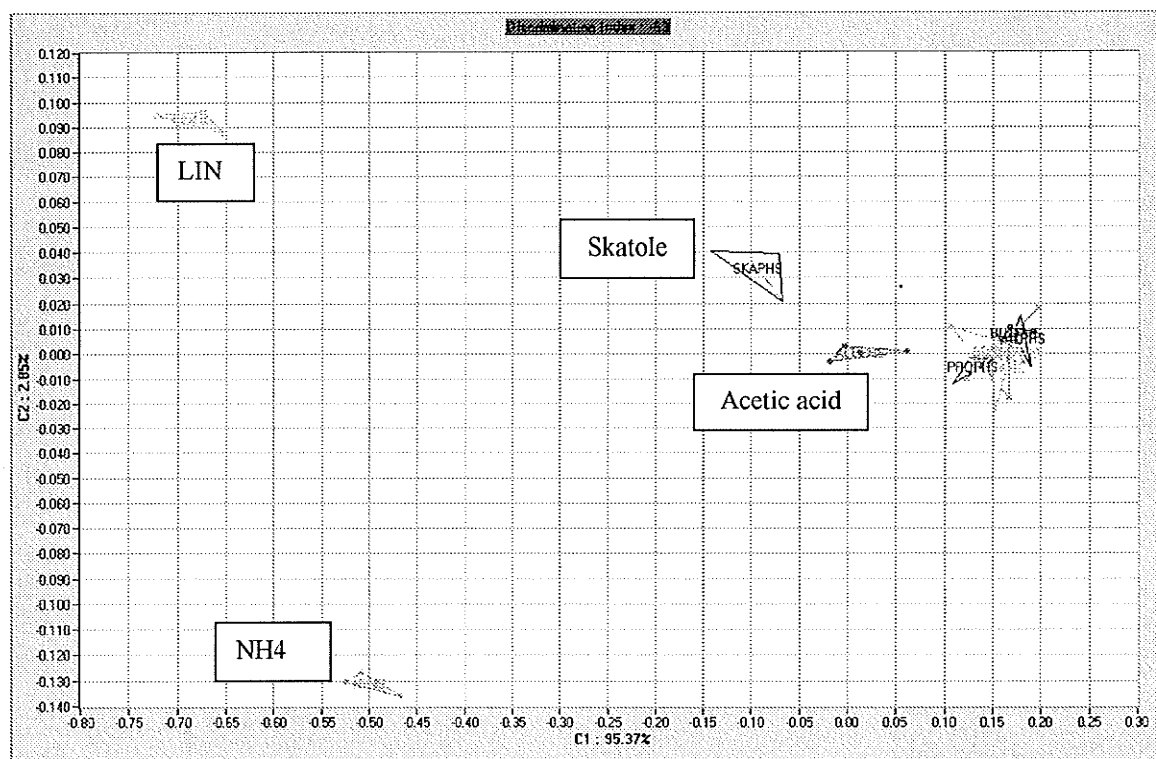


Figure 5.5 PCA map of the residual signals from linen (LIN) vs the residual from the individual SOS components.

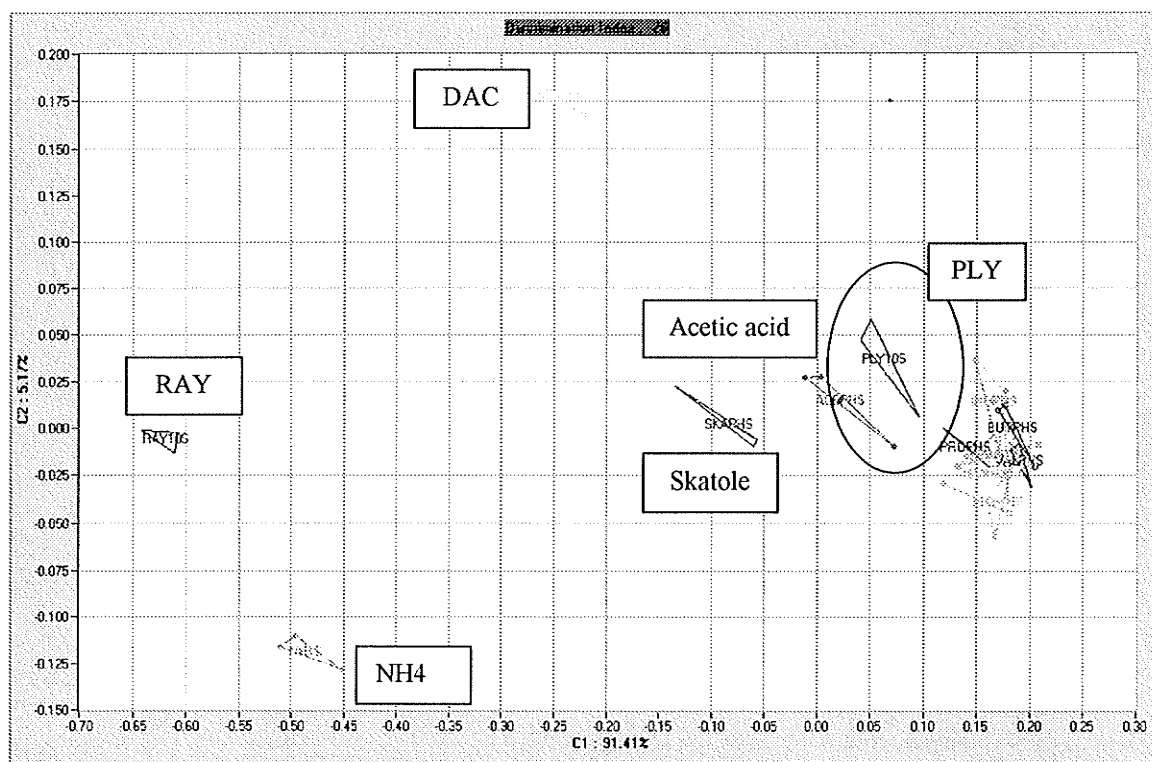


Figure 5.6 PCA map of the residuals of three synthetics: rayon (RAY), Dacron type 54 (DAC), and spun polypropylene (PLY) vs the residuals of the individual components.

In Figure 5.7 the residual signal for activated carbon cloth was shown with the residual signals for the individual components. The pattern showed the distance from ACC for all of the components, so one question which arose but which could not be answered in this data set was whether this was due to a dissimilarity of signal or of concentration of the signal.

These results allowed Hypothesis II to be accepted for all of the fabrics tested with the exception of spun polypropylene, which showed a unique pattern.

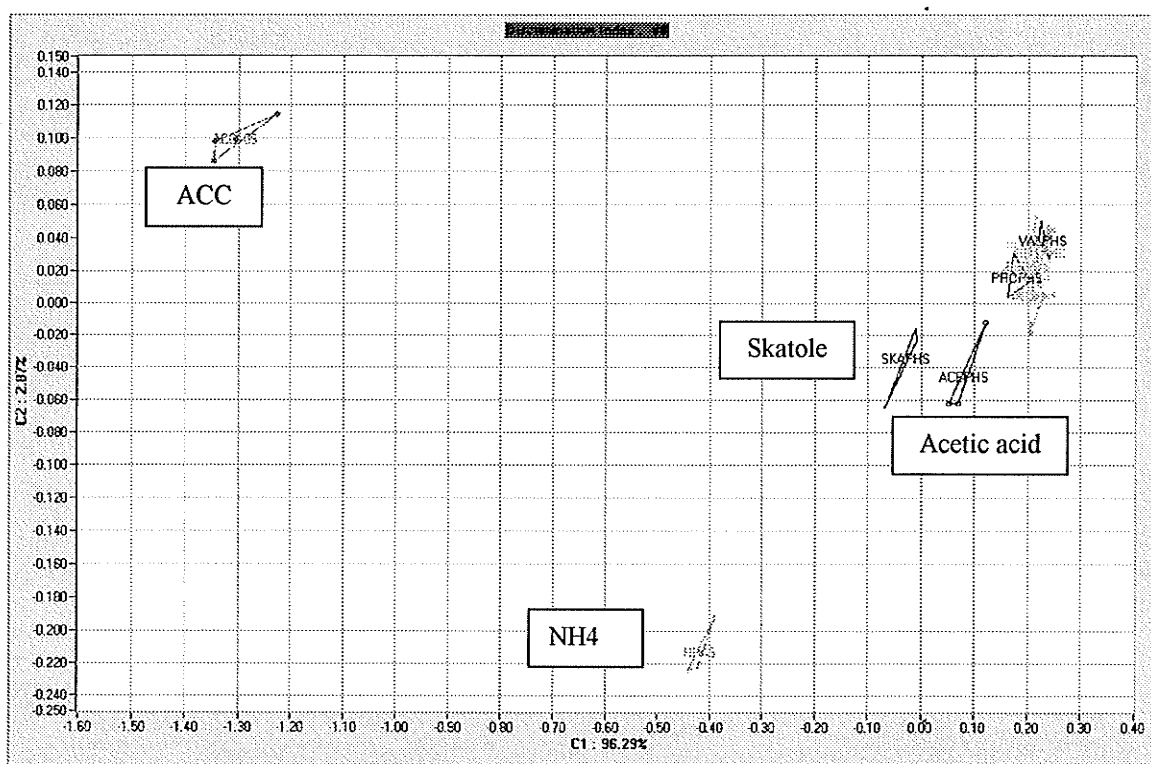


Figure 5.7. PCA map the residual signal for activated carbon cloth (ACC) vs the residual signal for the individual components.

5.3.3 Correlation of Electronic Nose Residuals with Sensory Data

Figures 5.8 and 5.9 are included to evaluate the relationship of the residual signals to the sensory means for each of the cloth swatches from the study in Study 2. Each figure includes two graphs, one (the upper graph) using the “Concentration Quantification” analysis in which the data was handled as a log scale and the other (the lower graph) using the “Sensory Score Correlation” analysis that used the data in a linear plot. Both methods provided a value for the correlation

coefficient (R) to evaluate the relationship. The values of the correlation coefficient in the Concentration Quantification analysis, were $R = 0.829$ for means from difference from control data and $r = 0.810$ for means from labelled magnitude scale data. This result showed little difference in the performance of the two scales, and a “reasonable” correlation between the signals and the sensory score for both methods. The values for the correlation coefficient were slightly lower, but similar for the Sensory Score Correlation analysis where $R = 0.777$ for the difference from control means and $R = 0.776$ for the labelled magnitude scale means.

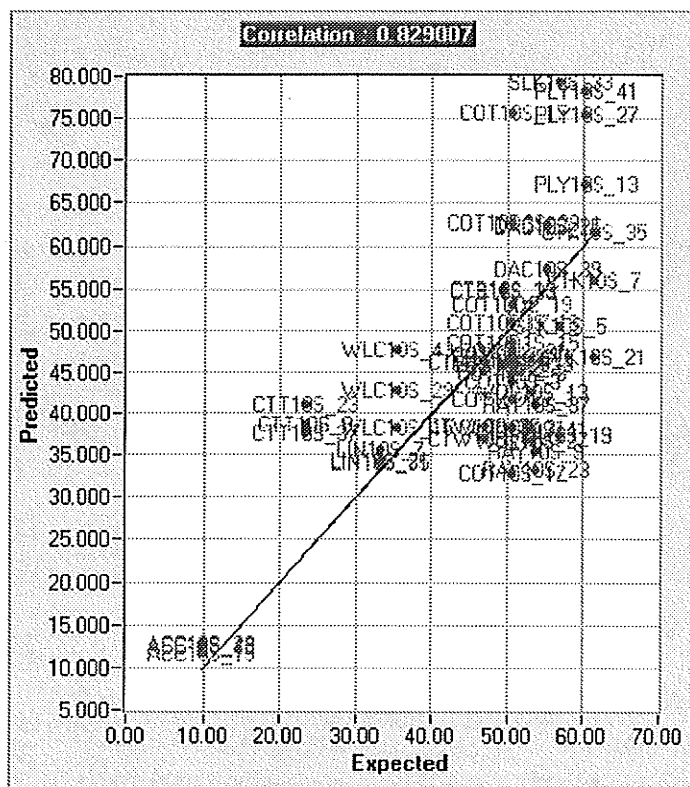
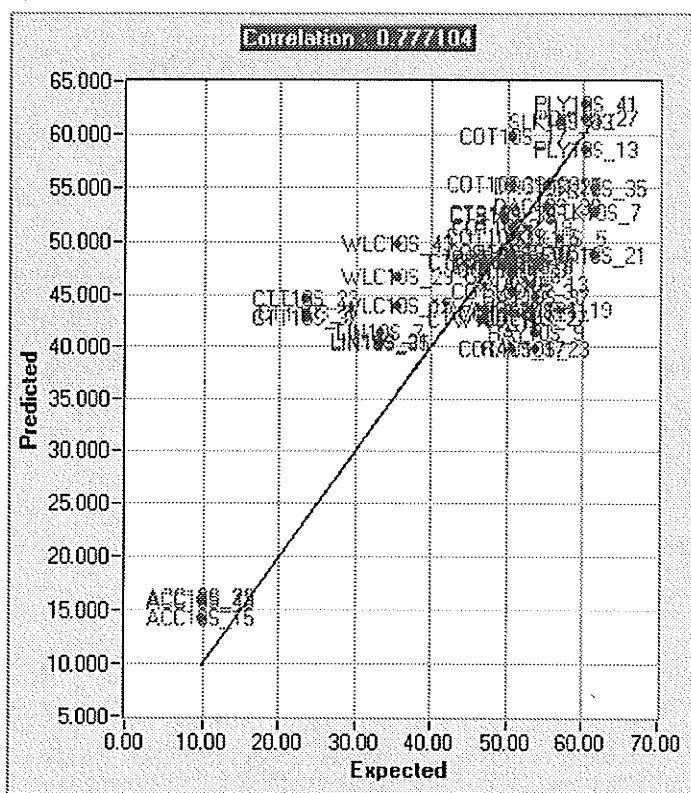


Figure 5.8 Graphs for Concentration Quantification (upper) and Sensory Score Correlation (lower) graphs for the cloth odor residual signals vs the difference-from-control (DFC) sensory means from Study 2.

Concentration quantification for all 13 fabrics residuals with DFC sensory means.

$R = 0.4973$ when ACC removed



Sensory Score Correlation for all 13 fabrics residuals with DFC sensory means.

$R = 0.5370$ when ACC removed

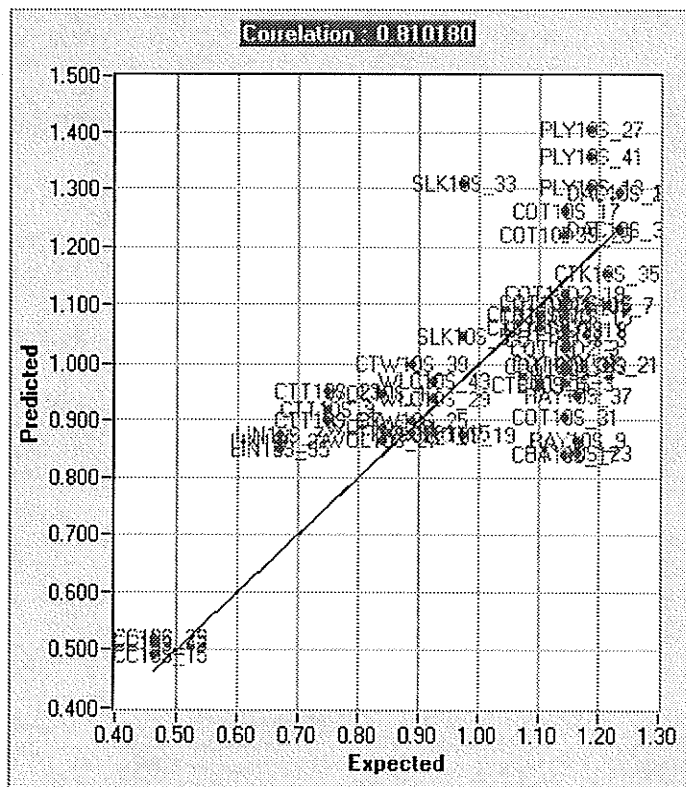
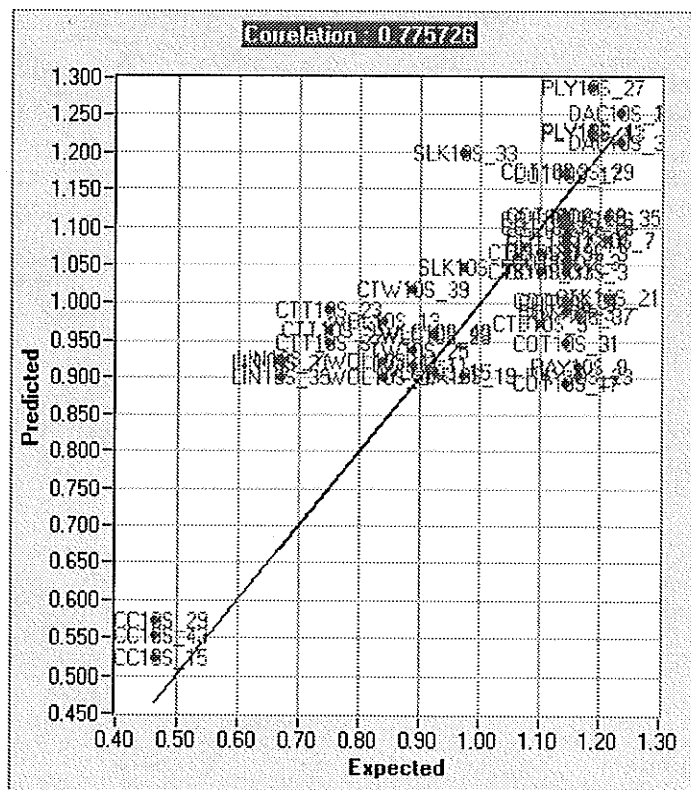


Figure 5.9 Graphs for Concentration Quantification (upper) and Sensory Score Correlation (lower) graphs for the cloth odor residual signals vs the labelled magnitude scale (LMS) sensory means from Study 2.

Concentration quantification for all 13 fabrics residuals with LMS sensory means.

R = 0.5819 when ACC removed



Sensory Score Correlation for all 13 fabrics residuals with LMS sensory means

R = .05977 when ACC removed

5.4 Conclusions

The GC/MS analysis component of this study was basically unsuccessful in answering the question, which components are adsorbed and released from the cloth during laboratory exposure of the cloth swatches. The equipment available for this work was not sensitive enough to establish a signal at the low levels of the odorants in the headspace. This can be studied at a future date using systems that are more suitable for this work, including SPME analysis and/or headspace mass spectroscopy.

Using the programming with the EN, the sample headspace could be evaluated separately from the cloth swatches. From the patterns of mapping in the PCA maps, the similarities of headspace could be demonstrated. While this result should be confirmed by further testing, the evidence was that the spun polypropylene sample gave a headspace sample that most closely resembled the components of the solution. The signals from ammonia, skatole, and acetic acid appeared to be different from the grouping of the other components and consistently mapped separately and closer to the residual signals from the various cloth swatches.

Chapter 6

Study #4: Field Testing and Electronic Nose Analysis of Selected Cloth Swatches

6.1 Introduction

The purpose of this work was to conduct actual field collections of odor on cloth swatches in a situation that would allow comparison to sensory data from human assessors and EN analyses of the samples. The opportunity to do this came in the form of an odor dispersion study being conducted by Dr. Q. Zhang and co-workers at the Department of Biosystems Engineering, University of Manitoba, beginning in summer 2003 and funded by the Manitoba Livestock Manure Management Initiative. An odor dispersion study was an expensive undertaking involving 15 panelists plus the team of workers conducting the study. The whole group must be transported some distance to an actual swine production facility for the actual testing. Panelists were selected and trained to use “magnitude matching” with the odor intensity of a scale of 1-butanol solutions to express the intensity of the odor perceived in the field. They must also cope with face masks to provide clean filtered air at all times they were not actually testing the ambient odors, walking through fields, and standing for extended periods, while the sensory data was collected.

This study provided an opportunity to collect odor on selected cloth swatches during the air dispersion study and to evaluate the swatches with the EN. The data were unique in that the swatch samples were generated while the odor intensity data were being collected and then data comparisons could be done between the sensory data and the EN data. This field test took the swatches out of the controlled laboratory environment and moved them into ambient weather conditions. There were differences in temperature, relative humidity, wind speed and location that could affect the way in which the odor was sampled onto the cloth. How this would affect the uptake of odor for the period of the exposure will be seen by the relationship to the intensity of the odor intensities assigned by the panel. The aspect of “breakthrough” could be a factor here

as well. This was the removal of adsorbed odor from the cloth by the action of the wind, so that the higher the wind speed the greater the breakthrough might be.

In order to conduct simultaneous sensory and fabric swatch testing, it was necessary to design and construct field vests to hold the fabric swatches while being worn by the field panelist. They had to be comfortable to wear over outdoor clothing and provide a means to attach cloth swatches to each of the field panelists using only the area of the front of the vest that would not be disturbed by the clipboards the panelists needed to record their sensory responses. These vests allowed the collection of ambient odor for the entire period at each exposure site (approximately 55 min at each session). The sensory data collected from the field panel would provide the numbers for the odor evaluation to correlate with the EN analysis at each of the sampling sites.

6.1.1 Objectives and Hypotheses

The overall objective of this study was to compare the results of electronic nose analyses of odor collection on cloth swatches under field conditions to simultaneous sensory analysis of those odor conditions during an odor dispersion study.

Hypothesis I: that the electronic nose sensor responses for the cloth swatches, when analyzed by principal component analysis mapping, would appear in a sequence which was related to the distance from the odor source.

Hypothesis II: that the mean sensory odor intensity values from the sensory responses in the field test were correlated with the electronic nose sensor responses of the cloth swatches collected at the same locations in the field.

6.2 Methods and Materials

6.2.1 Field Vests for Cloth Swatch Exposure during the Odor Dispersion Study

The field vest shown in Figure 6.1(a) was developed and constructed in this laboratory based on the recommended dimensions of a standard tabard design, which was then modified

completely to fulfill the requirements for testing. The fabric used was nylon rip-stop, which was purchased locally. It was chosen because of its strength and ease of handling for field use. The vest had six reinforced patches on the front with clips to hold the swatch sample and foil container in place during transport and wearing in the field. In all, 17 field vests were constructed to hold the cloth swatch packets during testing. Fifteen of these were assigned to the assessors for actual field exposure of the swatches. One was used as a reference standard, with the swatches receiving all the same handling treatment as the 15 field vests, but not being actually opened on site. The last one was used to sample odor at one of the outlet fans of the hog barn. This vest was held in place on a metal support approximately 3 m from the fan outlet (#1 on Figure 6.3(a)), and had the outlet air blowing on it for the same approximately 55 min sampling time. Another set of swatches was arranged on a metal support adapted from a portable table to hold samples downwind of the lagoon for the last sampling period. This set was constructed to be lower to the ground than the “fan” sample, but to be above the actual ground level. The support was placed on a plastic ground sheet to reduce any odor from this source.

The cloth swatches were contained in foil packets constructed from heavy-duty aluminum foil (Figure 6.1(b)). Packets were placed in random order for each set. Two samples of each of three fabrics were used each day for a total of 6 swatches. The protocol for handling the swatches is given in Figure 6.2, and panelists were trained in the handling of the swatches. The packets were only opened when panelists had reached their designated location in the grid and were closed before leaving that location. Samples were transported back to the laboratory on the vests to prevent any tearing of packets due to further handling under field conditions.

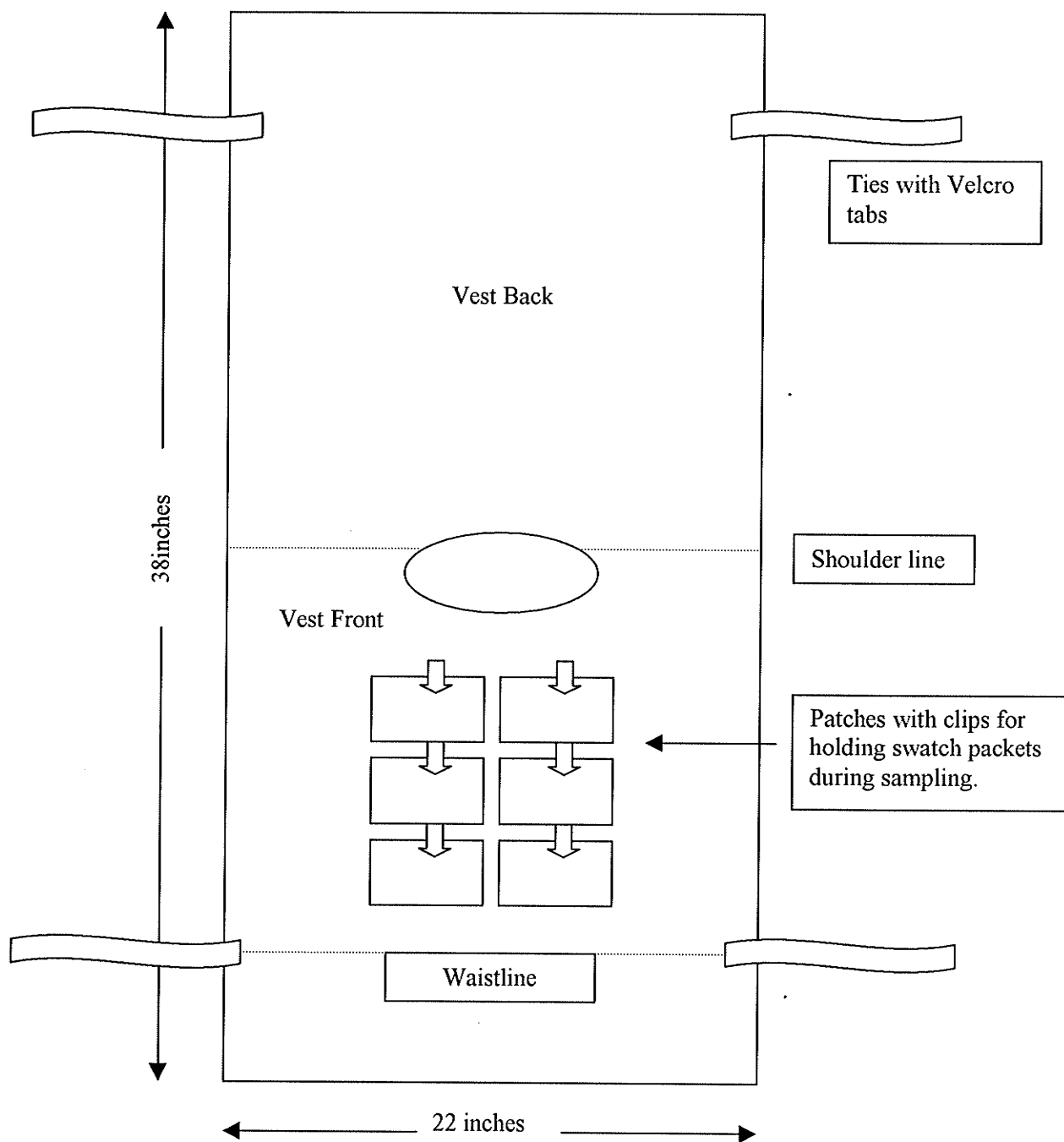


Figure 6.1(a). Field vest for odor sampling during data collection in the odor dispersion study. (not exactly to scale)

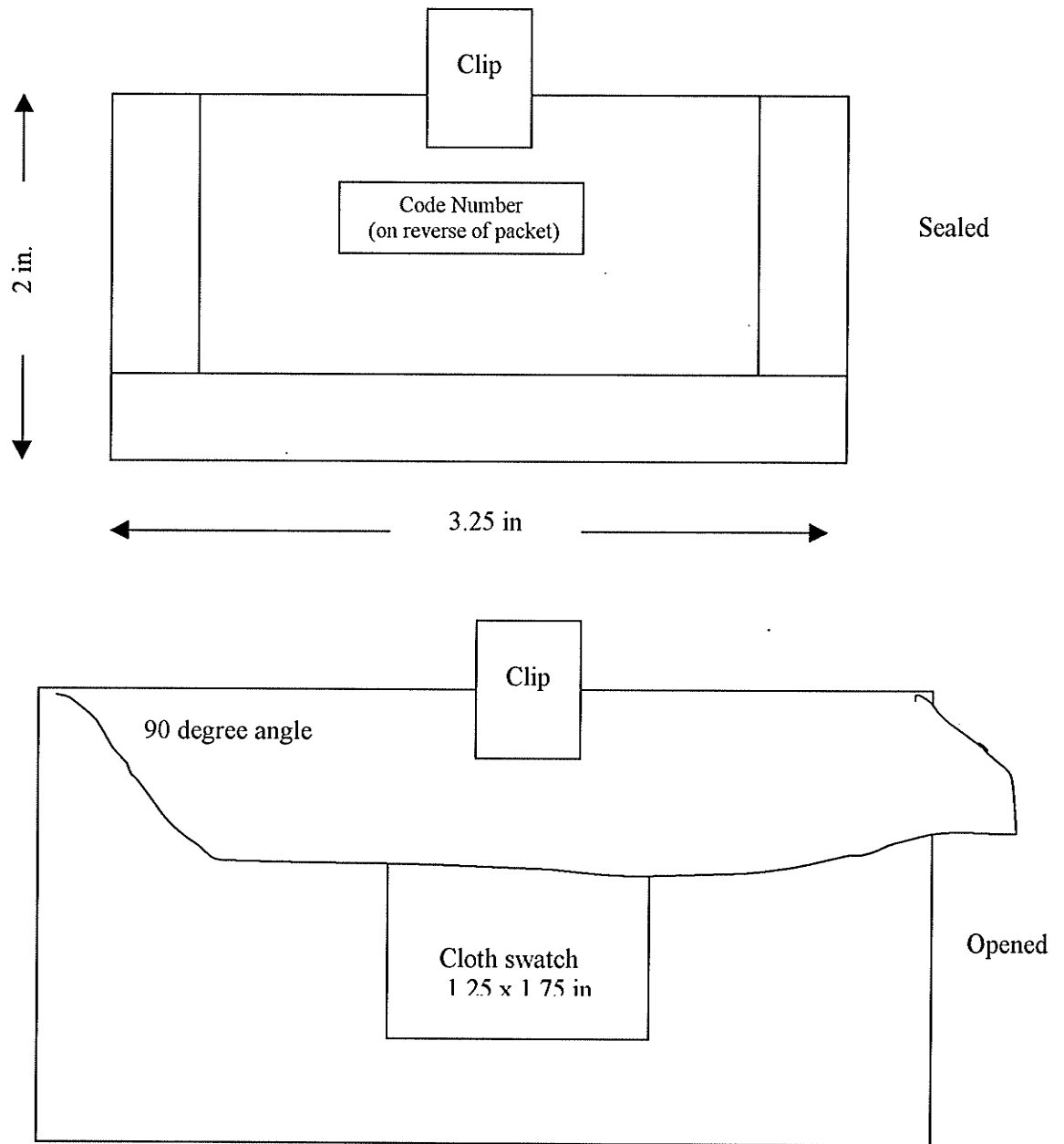
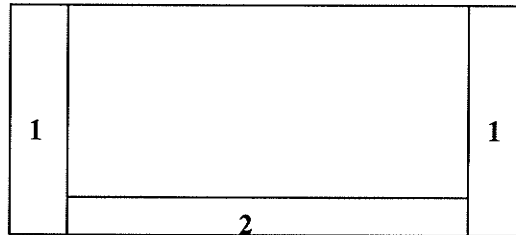


Figure 6.1(b). Aluminum foil packet containing cloth swatch. The packet is clipped to the vest at one of the holders and opened when the assessor reaches the designated vector location.

Opening and Re-sealing the Foil Packets on the Vest:



1. The packets containing cloth swatches are clipped to the vest and should not be removed. They will be removed back at the lab when the test is finished.
2. When you get to your field position, open the packets immediately before beginning the “sniffing” sequence #1 and leave them open until the end of sequence #3.
3. Open the packets carefully by folding back the side flaps (1) and then fold down the bottom flap (2). Lift the top layer to expose the piece of cloth and to create an “awning” to protect the swatch from your breathing. Try not to disturb the swatches while working on the sniffing sequence.
4. When the sequences are done, seal the packets before moving from your location. Flatten the top layer back down on the cloth, the re-fold the bottom and side flaps. Try to keep the package flat and well sealed to prevent any further exposure to air.

Many thanks for your help!

Figure 6.2 Instructions to panelists for handling the foil packets clipped to the field vest.

6.2.2 Field Testing

The field-testing was conducted by Zhou & Zhang (2004, personal communication). The 15 panelists were selected from students and staff of the University of Manitoba based on their ability to discriminate the odor of 1-butanol in an olfactometer presentation (Zhou & Zhang, 2004). This test was modified from the selection test in Study #2. The panelists each participated in six training sessions of 1-2 h each, during which they were given experience with the 1-butanol scale used for matching standards (Zhou & York, 2004 – unpublished data). Training sessions included evaluation of unknown standards with feedback of correct answers, discussion and time to review and reassess the samples. Unknowns using various concentrations of the swine odor simulant (Study #2) were also used for presentation, assessment and discussion. Training also included the “choreography” for handling the clipboards and facemasks worn in the field. The facemasks were 3M™ 6000 Series Half Face-piece masks equipped with 3M™ 6003 Organic Vapor/Acid Gas cartridge Filters. These provided the clean air for “rinsing” between assessments. Panelists were also trained to use the GPS units, which guided them to their sampling sites and provided the coordinates, which were recorded for each one. An experimenter controlled the timing for assessments by using walkie-talkies. When panelists were in place in the grid, timing began and one of the experimenters called sampling times at 10-s intervals, so that all assessments were done simultaneously at all grid points. The format of the grid used for odor sampling is shown in Figure 6.3(a), and the location of the “fan” and “lagoon” sampling site is shown in Figure 3(b). The weather conditions for each of the sampling days were recorded using an automated weather station (Zhou, 2004, personal communication) and the averages for the 1 h sampling periods are given in Table 6.3. Only one set of samples could be collected on each of the sampling days, even though two panels were conducted each day. The logistics of handling the packets under field conditions made on site changing of the sample sets impractical.

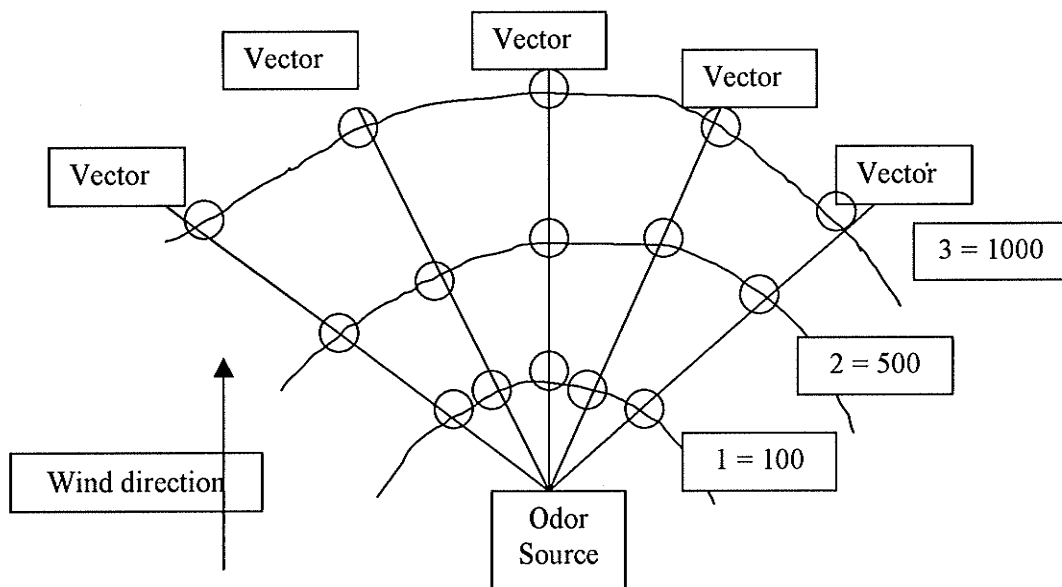


Figure 6.3(a). The field layout of the 15 assessors at the test location. An assessor is positioned at each intersection of a vector and a distance line. E.g. 1-2 is located on the second vector at 100 m.

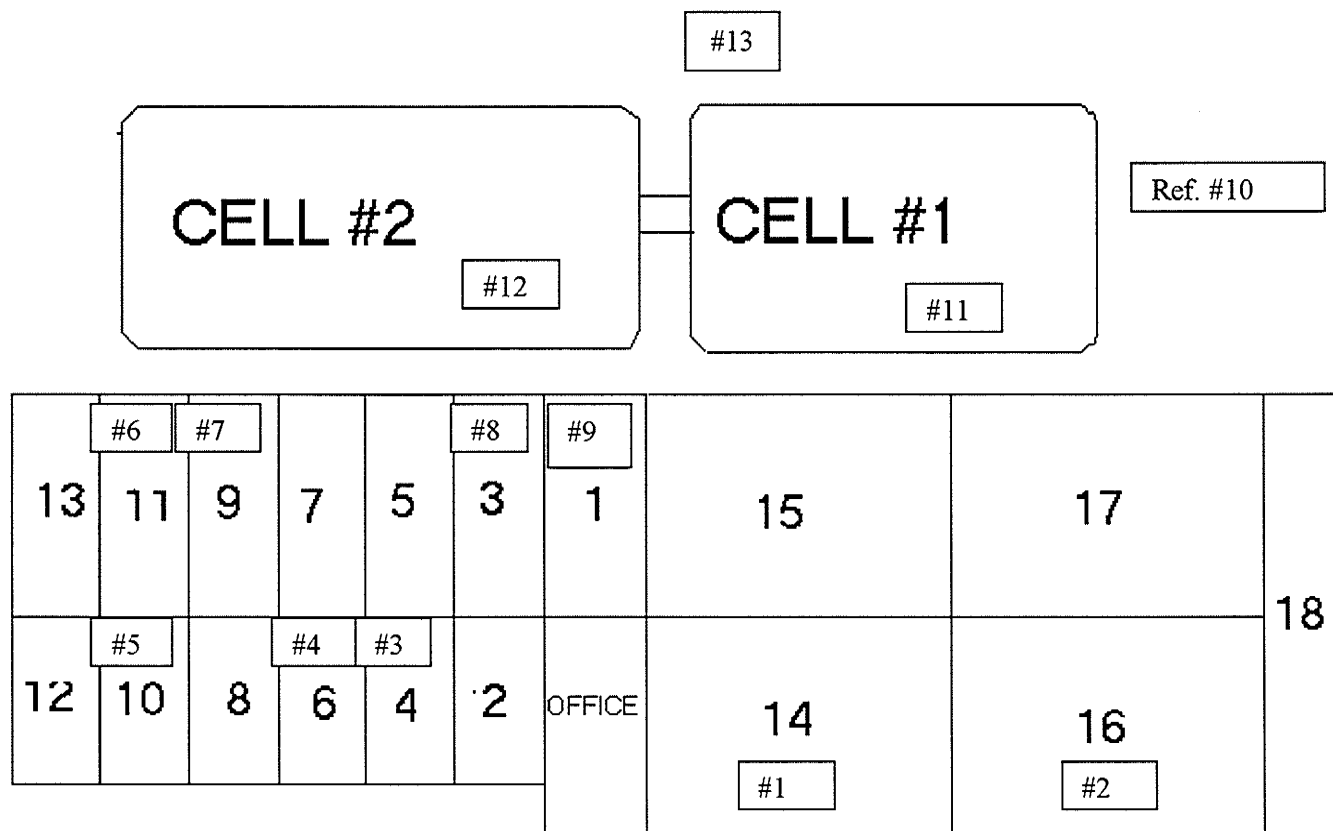


Figure 6.3(b). Farm layout for odor sampling site. #1 = “fan” sample for September 14 and 21, #9 = “fan” sample on October 5, and #13 = “lagoon” sample location on October 5. The wind-speed at the fan outlet was approximately 30 to 40 km/h (Source of diagram, Zhou, 2004, personal communication).

6.2.2.1 Odor Assessments

The ballot for field assessments is shown in Appendix J. It was designed to allow the odor intensity to be recorded as the intensity of the matching standard on the 1-butanol scale shown in Table 6.1. Odor assessments were recorded for 10 min, followed by a 10-min rest time. This sequence was repeated until three 10-minute sessions were recorded. Weather conditions during the field sessions were recorded using an automated weather station system (Zhou, 2004, personal communication).

6.2.3 Cloth Swatches for Field Testing

The selection of fabrics for testing was based on factors such as the ability to adsorb odors as shown in the results from Study # 2, the handling characteristics and the surface chemistry. The samples selected are shown in Table 6.2. Cotton flannel was included because of its use in other swatch studies, to provide some continuity in the sampling. Activated carbon cloth was included because of its ability to maintain odor adsorption and rayon because it was the base material for the production of activated carbon cloth. Spun polypropylene and Dacron were chosen because of their performance in Study #2, while the fabric which had score rankings of first for DFC and second for LMS, cotton knit, was not used because while it adsorbs odors well, it is very difficult to handle.

The cloth swatches for this study were of the same surface area as the circular swatches used in Study #2, but were cut as rectangular samples 1.25 in x 1.75 in. so that they could be fitted better into the foil packets.

Table 6.1 Concentrations of 1-butanol in the field scale used for magnitude matching of environmental malodors in this study.

"Field Panel" Sample Designation	1-Butanol Concentration ppm
1	120
2	240
3	480
4	960
5	1940
6	3880
7	7750
8	15550

Table 6.2 Planned field sampling times and identity of cloth swatches used for malodor sampling.

Date	Cloth samples used (DFC/LMS score ranking in M2)
September 14, 2003	ACC (13,13), PLY (2,3)
September 21, 2003	ACC, PLY, COT(7,5)
October 5, 2003	ACC, DAC (4,1), RAY (5,4)
Note: the abbreviations used for the cloth types are the same as for Study # 2	

6.2.4 Electronic Nose Analyses

The foil packets containing exposed cloth swatches were removed from the vests immediately on return to the laboratory that day, transportation time was 2-3 h. They were sorted and held in the foil packets until the next morning when they were placed into the 10 ml. auto-sampler vials with the most exposed face of the cloth oriented towards the inside of the vial. These were lidded immediately with magnetic caps lined with silicon/Teflon septa and crimped to seal.

Tests were conducted using an Alpha MOS Fox 3000 Electronic Nose equipped with 12 metal oxide sensors. Prepared samples were placed into a sampling tray for the auto-sampler. Samples were transferred sequentially to the incubator/heating block and gently agitated at

constant rpm/directional cycle to facilitate headspace sample production. The headspace sample (2500 μ l.) was drawn into the syringe and transferred to the injection port of the electronic nose. Data collection of sensor response was collected for 120 s followed by a 1080-s delay before injection of the next sample. The carrier gas (flow rate maintained at 150 ml per min) was oxygen/nitrogen at 20% $O_2 \pm 1\%$ (i.e. 19.8 to 20.2 % O_2) and with impurities specified as $H_2O < 5$ ppm, $C_nH_m < 5$ ppm, $O_2 + N_2 > 99.95\%$, $O_2 = 20\% \pm 1\%$.

The test conditions used for collection of electronic nose data were as follows:

incubation time:	15 min
incubation temperature:	40°C
acquisition time:	2 min
delay time (sensors restored to “zero” state):	18 min
carrier gas flow rate:	150 ml/min

To evaluate any advantage to using a higher temperature for incubation, the swatches collected on September 14 were re-run at 60°C for 15 min.

As stated above, the cloth swatch had the same exposed surface area as the circular samples used previously, but were cut as rectangles that had the same surface area plus a small amount (approximately 6 mm) for space for the clip. This area was covered by the foil during swatch exposure in the field.

6.2.5 Data Analysis

The data readings for each person/grid location were recorded as the value on the 1-butanol magnitude matching scale that was assigned at each evaluation. Principal components analysis (PCA) was performed on the EN sensor readings using the algorithms in AlphaSoft Version 8. The individual sensory readings were used to plot “vector graphs” for each of the grids on each of the sampling days to help to visualize what was actually happening in each odor plume during the test using Microsoft Excel 97. The sensory data were used in combination with the electronic

nose readings to evaluate the presence of any correlation between the two forms of data through the calculation of values that could be used in the AlphSoft Version 8 Sensory Score Correlation algorithm with the sensor readings. Various averages were calculated to reflect the plume of odor to evaluate the degree to which the odor adsorbed by the swatch correlated with the sensory scores assigned at that location.

6.3 Results and Discussion

6.3.1 Field Sampling Conditions

The weather conditions for each of the sampling days are shown in Table 6.3. The temperatures were within a narrow range from 11 – 15.1°C. The relative humidity varied from approximately 50% on the last day of testing to 82.8% and 92.2% on the other two days. The wind speed (km/h) was greatest on Sept 21, 2003. These conditions compared to the laboratory conditions for swine odor simulant exposure where the temperature was 20 - 22 °C, the relative humidity was ambient and dependent on the season, and the exposure rate of 2L/min corresponded to a calculated wind-speed of 3.8 km/hr. The swatches were exposed to much higher wind speed under field conditions than under laboratory conditions, and this could affect the phenomenon of “breakthrough”, which will be part of the discussion.

Table 6.3 Average weather conditions during actual field sampling (for 1 hour from start time)				
Test Date	Time of day – start time	Temperature (°C)	Relative humidity (%)	Wind speed (km/h)
September 14/03	11.00	13.7	82.8	11.1
September 21/03	15.10	11.0	92.2	21.7
October 5/03	12.01	15.1	51.7	15.8
Source of weather data: Zhou, Xiaojing (2003) personal communication.				
Note: the wind-speed during field sampling compares to a calculated “wind-speed” of 3.8 km/h through the Gilair pump used for laboratory exposures to the swine odor simulant.				

6.3.2 Vector Graphs

A series of what are termed here as “vector graphs” are shown in Appendix K. These graphs showed the time versus odor intensity responses for each of the grid locations on each of

the sampling days, with each individual graph representing the three positions on one of the vectors shown in Figure K.1. The purpose of these graphs was to represent the odor stimuli being rated by the assessors. This was needed as a tool to aid in developing some ideas as to how these numbers can be converted into a meaningful overall number that can be used to relate these assessments to the sensor readings in the electronic nose analyses.

- On September 14 (Figure K.1), the odor plume was strongest on the first two vectors for the 100-m positions, intermediate for the two farther positions, and weaker for all distances on the third, fourth and fifth vectors.
- On September 21 (Figure K.2), the 100-m positions showed high levels of odor, while vectors 1 and 2 showed almost none at the two farther positions. Vectors 3 and 4 showed intermediate odor levels at the 500-m positions and low levels at the 1000-m positions. Vector 5 showed high levels of activity at 100 m and low to intermediate levels at the 500-m and 1000-m positions.
- On October 5 (Figure K.3), the first and second vectors showed almost no odor intensity for all three distances. The third, fourth and fifth vectors all showed moderate intensity for the 100-m positions. The third vector showed very low intensities for the 500-m and 1000-m positions. The fourth and fifth vectors showed low to moderate intensities for the 500 m positions and did not have assessors in the 1000-m positions.

These graphs showed how variable the odor plume could be so that the cloth swatch is being exposed to varying odor levels instead of the constant exposure of the laboratory test, with levels often varying widely.

6.3.3 Odor Intensity Data

These data were collected as magnitude matching to an intensity scale, which is a log-spaced series of 1-butanol concentrations from 120 to 15,500 ppm and with eight concentration steps plus a “0” response, for a total of nine possible responses. Examples of the methods by

which odor dispersion data could be analysed are given by Guo et al. (2001) and Zhu & Li (2000). In these cases, the data were converted into geometric means for use in data analysis. In the current study being conducted by Zhang & Zhou (2004, personal communication), the data were being used in the form of geometric means of the 10-min test periods.

The summary of the sensory data and all of the variations on the mean, which were calculated for this data for this study, are given in Table 6.4. These values were used to relate the sensor readings for each of the swatches on each of the sampling days to the sensory perceptions of odor. There was no standard method of analysis of this type of data, and this range of trials clarified any patterns that might be present.

Table 6.4 Summary of sensory data collected during three field sessions. September 14/2003							
Position	# of readings (A)	# of readings not "0" (B)	Total of Sensory Scores Assigned (C)	Sensory Score Arithmetic Mean #1 (C/A)	Sensory Score Arithmetic Mean #2 (C/B)	Maximum assigned sensory score	Sensory Score Geometric Mean (using only scores not "0")
1-1	183	183	1100	6.01	6.01	8	5.96
1-2	183	183	670.5	3.66	3.66	5	3.61
1-3	183	181	244	1.33	1.35	3	1.27
1-4	183	149	184	1.00	1.23	6	1.12
1-5	183	140	220	1.20	1.57	5	1.34
2-1	181	181	647	3.57	3.57	5	3.43
2-2	183	73	87	0.47	1.19	3	1.13
2-3	176	107	167	0.95	1.56	5	1.29
2-4	180	11	11	0.06	1.00	1	1.00
2-5	183	182	368	2.01	2.02	4	1.83
3-1	183	178	715	3.91	4.02	7	3.65
3-2	182	182	541	2.97	2.97	5	2.90
3-3	183	110	134	0.73	1.22	2	1.16
3-4	183	42	44	0.24	1.05	2	1.02
3-5	182	182	203	1.12	1.12	3	1.08

September 21/2003

Position	# of readings (A)	# of readings not "0" (B)	Total of Sensory Scores Assigned (C)	Sensory Score Arithmetic Mean #1 (C/A)	Sensory Score Arithmetic Mean #2 (C/B)	Maximum assigned sensory score	Sensory Score Geometric Mean (using only scores not "0")
1-1	183	160	799	4.37	4.99	8	4.45
1-2	183	183	1241	6.78	6.78	8	6.75
1-3	183	183	1240	6.78	6.78	8	6.75
1-4	182	182	1157	6.36	6.36	8	6.30
1-5	183	183	1012	5.53	5.53	8	5.35
2-1	183	0	0	0	0.00	0	0.00
2-2	122	22	47	0.38	2.14	4	1.94
2-3	183	178	706	3.86	3.97	6	3.67
2-4	141	130	475	3.37	3.65	6	2.40
2-5	122	91	248	2.03	2.73	5	2.36
3-1	122	5	5	0.04	1.00	1	1.00
3-2	152	22	22	0.15	1.00	1	1.00
3-3	183	88	127	0.69	1.44	4	1.18
3-4	182	123	209	1.15	1.70	4	1.49
3-5	180	167	383	2.13	2.29	4	1.97

October 5/2003

Position	# of readings (A)	# of readings not "0" (B)	Total of Sensory Scores Assigned (C)	Sensory Score Arithmetic Mean #1 (C/A)	Sensory Score Arithmetic Mean #2 (C/B)	Maximum assigned sensory score	Sensory Score Geometric Mean (using only scores not "0")
1-1	183	5	7	0.04	1.40	2	1.32
1-2	182	37	44	0.24	1.19	2	1.12
1-3	181	174	522	2.88	3.00	5	2.65
1-4	180	179	544	3.02	3.04	5	2.88
1-5	182	182	727	3.99	3.99	5	3.88
2-1	183	1	1	0.01	1.00	1	1.00
2-2	183	21	21	0.12	1.00	1	1.00
2-3	183	11	12	0.07	1.09	2	1.12
2-4	183	82	134	0.73	1.63	4	1.46
2-5	183	97	146	0.80	1.51	3.5	1.23
3-1	179	62	80	0.45	1.29	3	1.20
3-2	183	4	4	0.02	1.00	1	1.00
3-3	183	4	5	0.03	1.25	2	1.19
3-4	No panelist present						
3-5	No panelist present						

6.3.4 Electronic Nose Analyses

The standard protocol was that all samples would be analyzed within the shortest time to attempt to no changes. The practical length of the “immediate” time frame was dictated by the sampling rate of the electronic nose (3 samples per hour) and the number of samples to be analyzed in a given set. The unit was capable of running overnight unsupervised, and this was utilized to complete the analyses within one day of preparation. In the previous studies, samples were all analyzed within 1 day of exposure of the swatch to the odor source. The 1-day time frame was the plan for this study as well and was carried forward for the first sampling day, which was called the “pretest”. Up to this point, no analyses had been done of changes in odor signal versus time for the electronic nose, (i.e., of the stability or substantivity of the odor on the cloth swatches), so no longer-term stability was assumed for this study.

There were some unanticipated events during and after the pretest that affected the electronic nose analyses of these subsequent samples. First, there were the observations on holding samples in the pretest, that the activated carbon cloth swatches were found to have etched the foil somewhat when held in the foil packets. In subsequent sampling days, this was taken into account and the samples taken out of the foil immediately and sealed in the vials. Any effect this might have had could not be completely evaluated due to the autosampler difficulties. The second major event occurred on beginning the analysis of the September 21 samples when the HS-50 autosampler ceased functioning permanently. This resulted in several unsuccessful days of trying to get the system to work. This breakdown resulted in the need to install the new system (an HS100 autosampler), reprogram the computer and test the system. The replacement of the autosampler took until October 8, at which point the diagnostic program was run successfully before continuing the other samples.

The effects on the sampling and analysis times are shown in Table 6.3. The factor of holding times introduced a variable into this study that could not be separated from the treatments and that could not be accommodated by running more field samples. The lateness of beginning

the field season and the onset of cold weather made these times the only field test days available. In order to evaluate the effect of these delays, the plans for the next study had a substantivity component added to test the effect of holding times on the stability of the electronic nose sensor readings over a 16-day holding period. The electronic nose results shown below refer to the results of this work, which is reported in Chapter 7.

The actual test dates, cloth swatches (with their rankings in the Study # 2 tests) and the actual holding delays for each are shown in Table 6.5. The results from September 14 (the “pretest”) were the only ones that were obtained within the 1-day time frame, which was the standard test protocol here.

Figure 6.4 shows 2 principal components analysis maps: the upper one contains the data from the three distances, the control sample and the “fan” sample for activated carbon cloth. The electronic nose was able to discriminate among all of the sample groups, although the discrimination index (for which the maximum value = 100) is only discrimination index = 59. Some interesting points were shown here. Firstly, there was the correct sequencing of the three distances and the control sample with the ACC1 being 100 m from the odor source, ACC2 being 500 m from the odor source, ACC3 being 1000 m from the odor source and the ACC0 control sample not exposed to the field odor. The ACCF sample taken at the fan mapped very closely to the unexposed controls and the 1000 m samples, which was likely due to “breakthrough” (the physical removal of the odorant from the surface by wind action) given the fan speed (approximately 30 to 40 km/h) and the close distance of the swatches to the fan.

This set of samples was also tested at an incubation temperature of 60°C for the 15-min incubation time, to see if there was any improvement in the results from the samples. This is shown as the lower principal component analysis map in Figure 6.4. and shows no differentiation by distance. When this analysis was done for the spun polypropylene samples, the same lack of differentiation occurred. This lack of differentiation indicated that the quality of the data was

diminished by this change in the temperature program, and subsequent testing was done using only the 40°C/15-min incubation as in Study # 2.

Table 6.5 Field-sampling times, cloth swatches used for malodor sampling and analysis times for this study.		
Date	Cloth samples used (DFC/LMS score ranking in Study # 2)	EN analyses
September 14, 2003 (initially the "Pretest")	ACC (13,13), PLY (2,3)	Analyzed immediately using the HS-50 auto-sampler (i.e. within 1 day)
September 21, 2003	ACC, PLY, COT(7,5)	Samples sealed in vials on September 21 for ACC and September 22 for PLY and COT, then held at room temperature away from light. Analyzed after the HS-100 auto-sampler was installed. (Holding times - 20 and 21 days – two days required to complete all of the samples.)
October 5, 2003	ACC, DAC (4,1), RAY (5,4)	Samples sealed in vials October 5 and held as for September 21 samples until new auto-sampler installed. (Holding times - 4 and 5 days – two days required to complete all of the samples.)
Note: the abbreviations used for the cloth types are the same as for Study # 2		

Figure 6.5 shows the PCA maps of the spun polypropylene samples for September 14. The upper graph includes all of the samples plus the control and the "fan" sample. Once again the "fan" sample maps near the unexposed control, while the three distances form a pattern as for the activated carbon cloth samples. One exposed sample, PLY24, maps in the control sample area. This sample was taken at 500 m on Vector 4, and as can be seen in Figure 6.4, this vector showed almost no exposure to the odor plume. The maximum sensory score assigned at this grid-point was "1"; so, this "exposed" sample should have shown no odor present, and it didn't. The results for these two fabrics allow Hypothesis I to be accepted for the September 14 data.

To evaluate the effect of vectors on electronic nose analysis, the data from September 14 was re-coded so that the principal components analysis algorithm would read the vector rather

than the distance as the coding characteristic. The principal components analysis maps for this analysis are shown in Figure 6.6. For both the activated carbon cloth (upper) and spun polypropylene (lower) principal components analysis maps, contrary to the results for distances, there was no useful distinction for the different vectors in this data set.

September 14, 2003 - Pretest

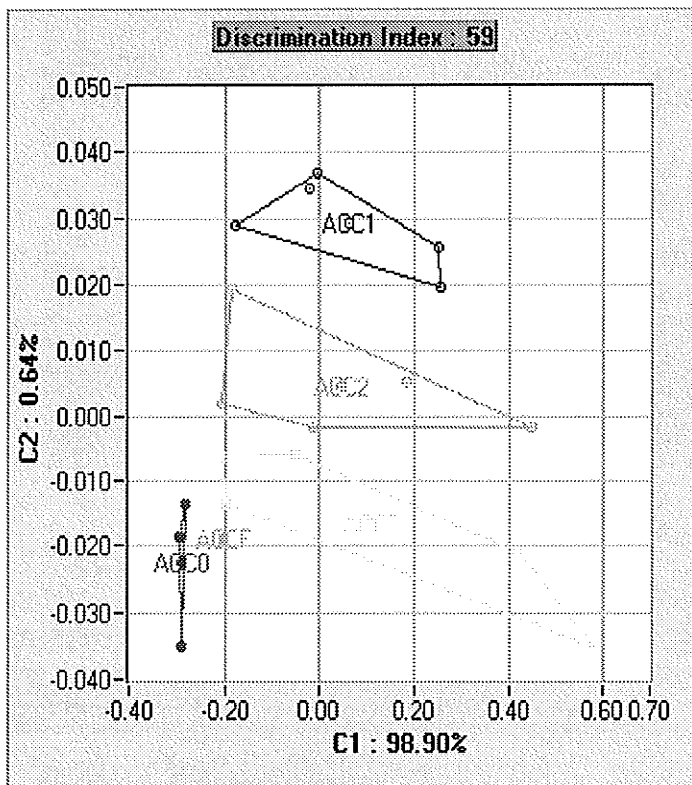
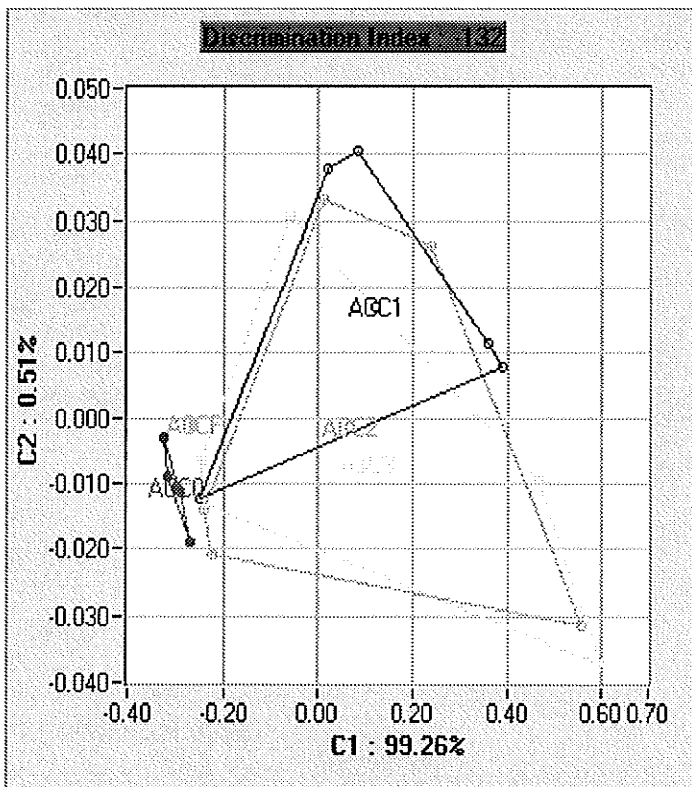


Figure 6.4 PCA map of ACC by distance on September 14/03

ACC1 – 5 samples
ACC2 – 5 samples
ACC3 – 5 samples
ACC0 – 3 samples
ACCF – 1 sample

There is separation between the three distances over all of the vector points. The samples from the 1000 m group are closest to the unexposed sample. The sample which was exposed to the output from the fan maps near these as well – which would not be expected from the intensity of the odor at the outlet where the fan is placed. This may be an artifact of breakthrough due to the velocity of the air at the point of sampling.



PCA map of ACC on September 14/03 of samples incubated at 60°C for 15 min. This change in the temperature decreased the differentiation among the samples. The same result was obtained with the PLY samples. For this reason, the remaining samples were analyzed only at the 40°C incubation temperature.

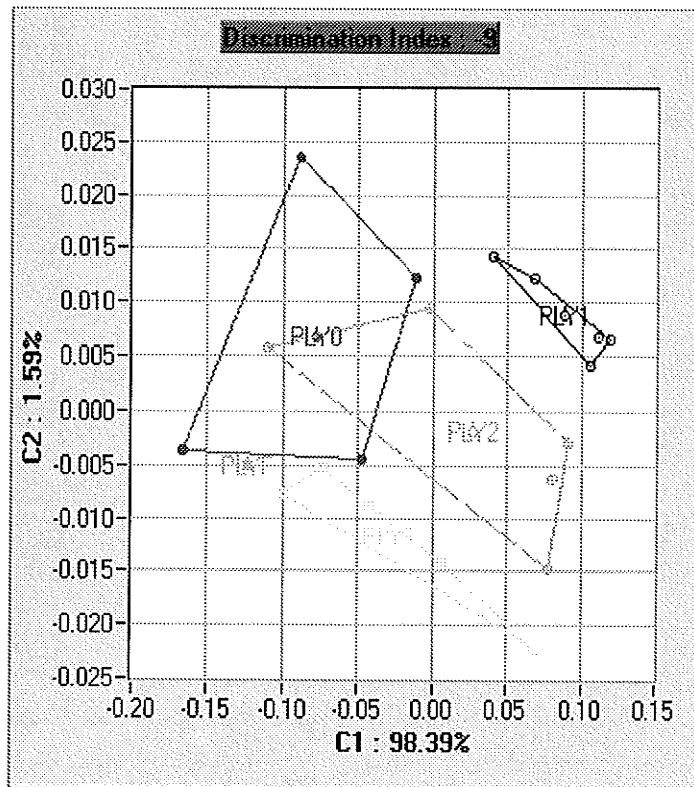
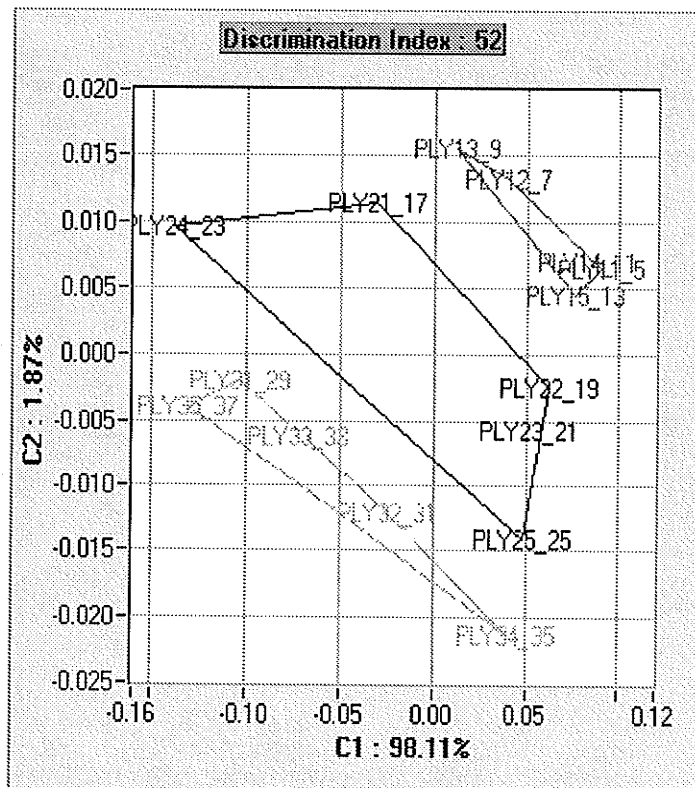


Figure 6.5. PCA map of PLY by distance on September 14/03

The upper map contains the results of the samples incubated at 40°C for 15 min. There is separation between the three distances over all of the vector points. PLY0, the unexposed sample shows positioning which may be due to the presence of its own unique odor which the EN is measuring in the absence of malodors from the field sampling. Also the PLY24 sample (shown in the lower map is mapping with the PLY0 sample – and this sample was located at a point with almost no odor plume for the sampling period. Again, the sample which was exposed to the output from the fan maps near the samples from 1000 m – which would not be expected from the intensity of the odor at the outlet where the fan is placed. This may be an artifact of breakthrough due to the velocity of the air at the point of sampling.



The lower map shows the clear differentiation of distances when the other samples are removed.

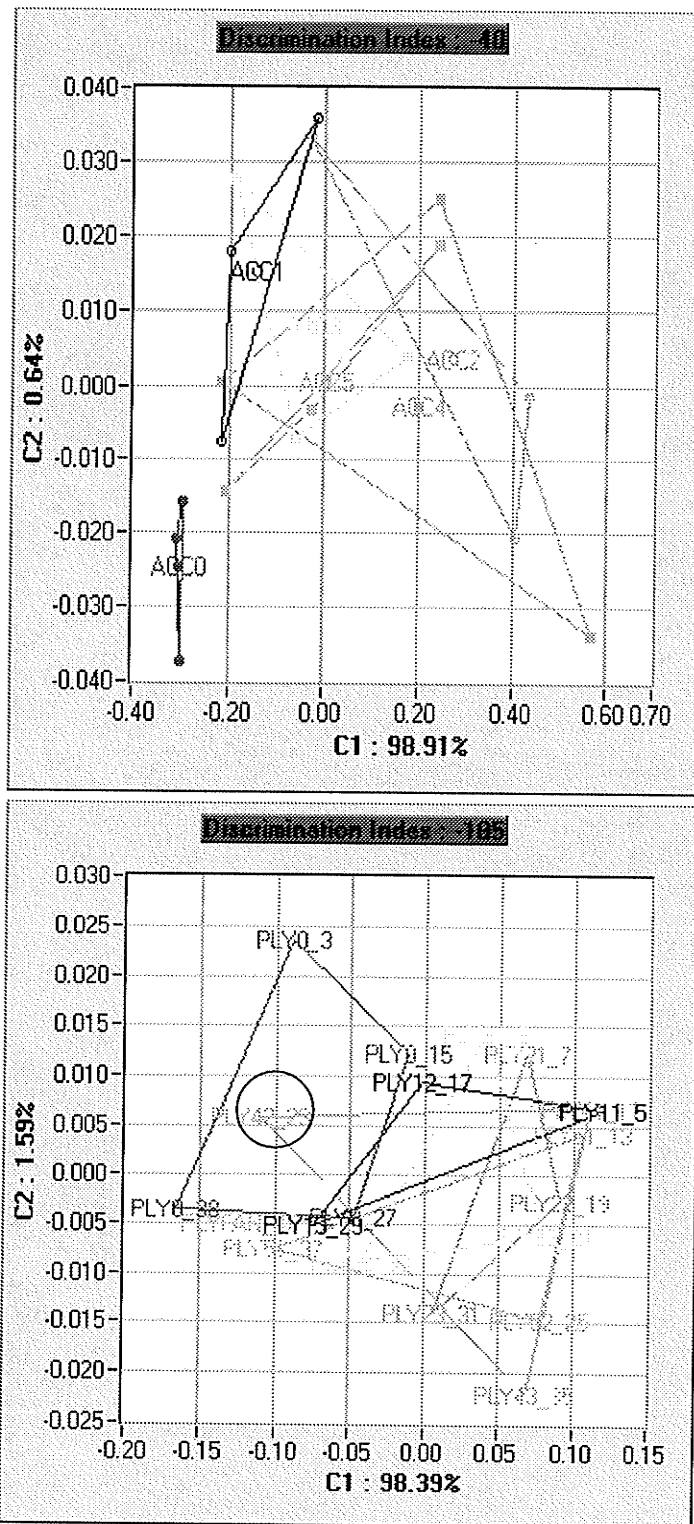


Figure 6.6. PCA map of ACC and PLY swatches by vector for September 14 testing.

The upper map contains the results from ACC and the lower map from PLY. There is differentiation between the unexposed control and the exposed swatches, but there is no pattern for the vector responses compared to each other. The PLY 24 sample (circled) – now coded PLY42 – again maps with the PLY0 sample.

The following PCA maps are Figures 6.11 to 6.16 containing the results for the fabric swatches from September 21 and October 5 coded for distance:

Figure 6.7 – ACC activated carbon cloth – September 21

Figure 6.8 – PLY spun polypropylene – September 21

Figure 6.9 – COT cotton flannel – September 21

Figure 6.10 – ACC activated carbon cloth – October 5

Figure 6.11 – DAC Dacron type 54 – October 5

Figure 6.12 – RAY rayon (spun viscose challis) – October

Each of the figures contained two principal components analysis maps, with the upper one being the map with all of the samples and the lower one with the “fan” sample and “fan” and “lagoon” samples removed. None of these maps showed any useful differentiation and all of them were prepared from samples that were stored 20-21 days for the September 21 samples and 4-5 days for the October 5 samples. As is seen later in the work on substantivity in Study #5/Chapter 7, the samples deteriorated on storage and the likelihood of getting useful data from them diminished. No conclusions were, therefore, drawn from these maps.

September 21, 2003

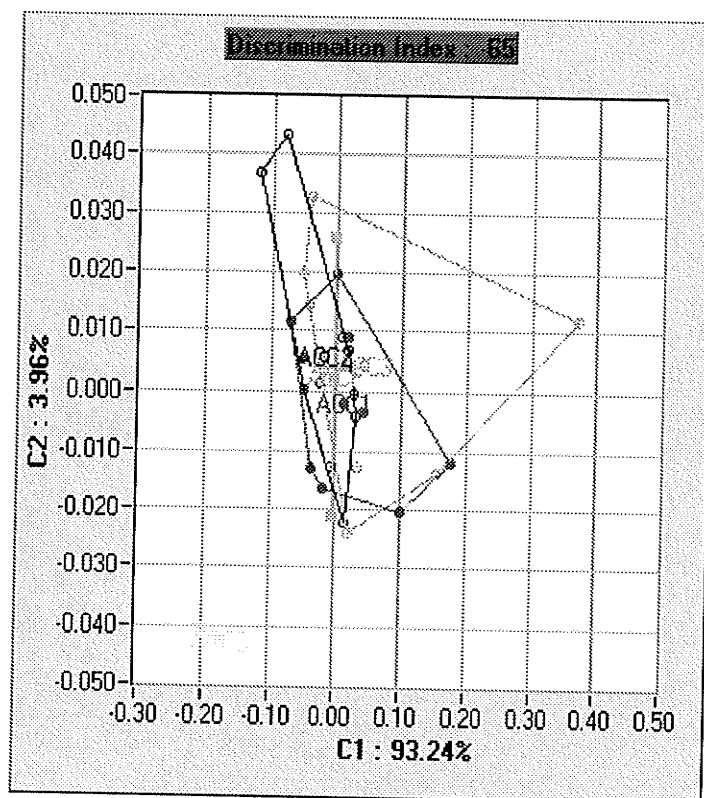
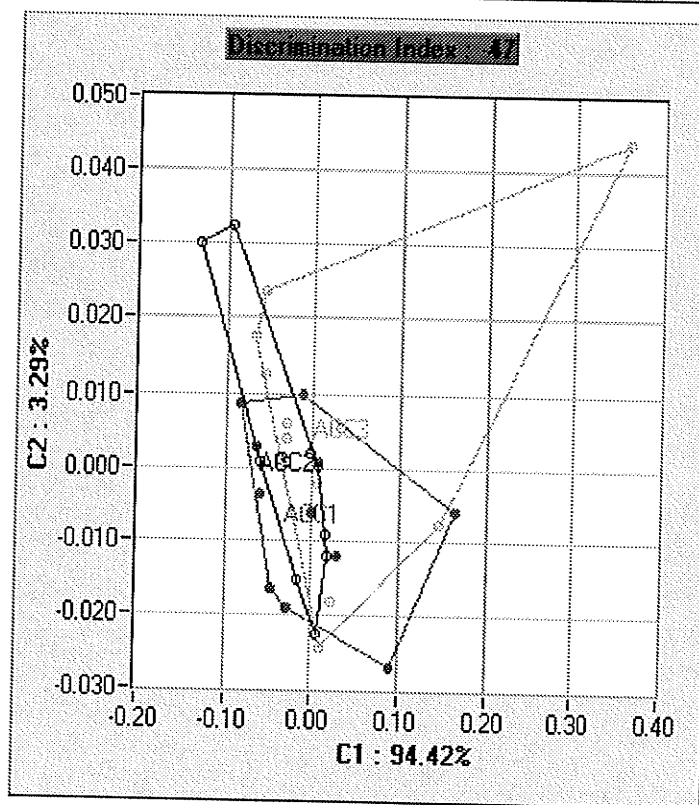


Figure 6.7 PCA map of ACC data from September 21 analyzed by distance from the odor source.

There is no useful differentiation in this data presumably due to the holding time before sample analysis – due to the breakdown of the autosampler component of the EN system.



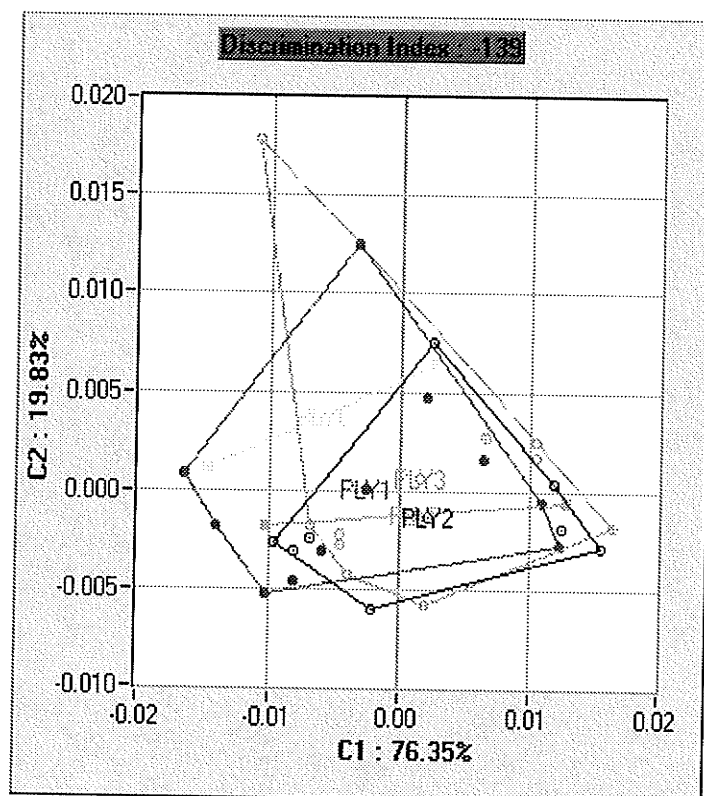
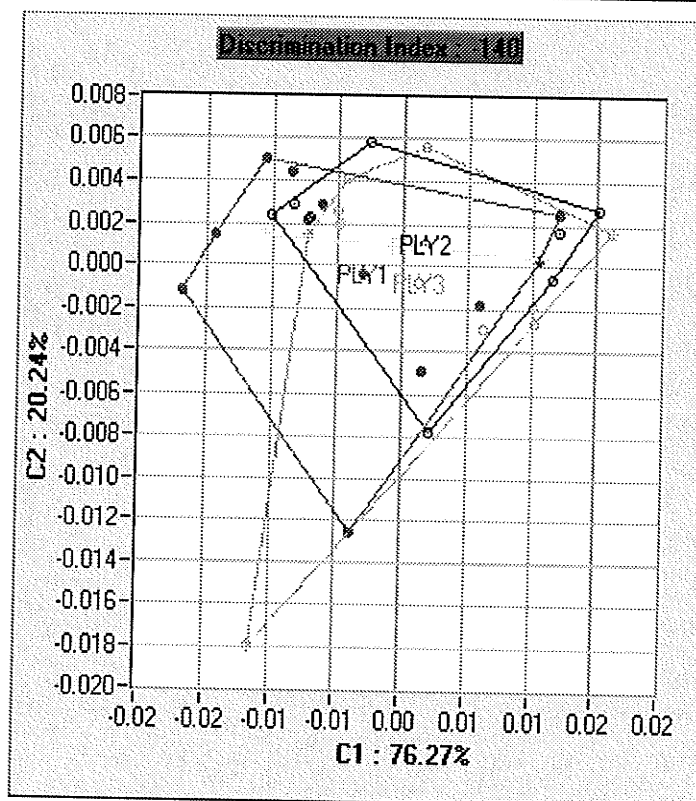


Figure 6.8. PCA map of PLY data from September 21 analyzed by distance from the odor source.

There is no useful differentiation in this data presumably due to the holding time before sample analysis – due to the breakdown of the autosampler component of the EN system.



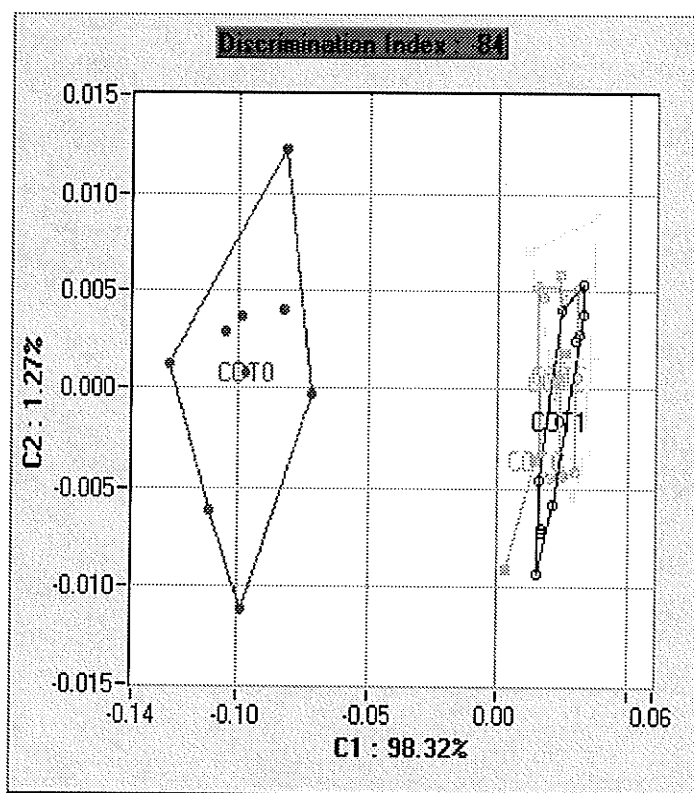
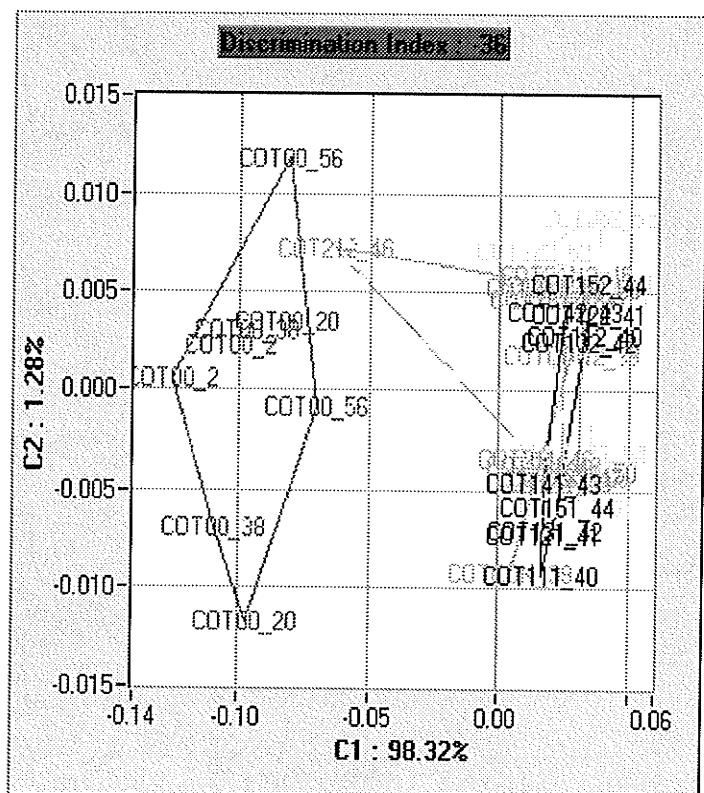


Figure 6.9. PCA map of COT data from September 21 analyzed by distance from the odor source.

There is no useful differentiation in this data presumably due to the holding time before sample analysis – due to the breakdown of the autosampler component of the EN system.



October 5, 2003

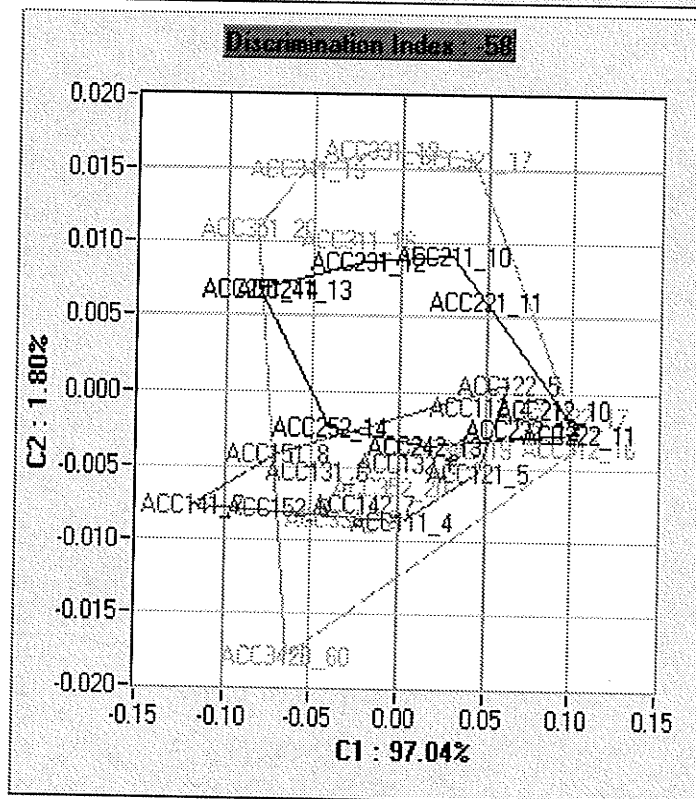
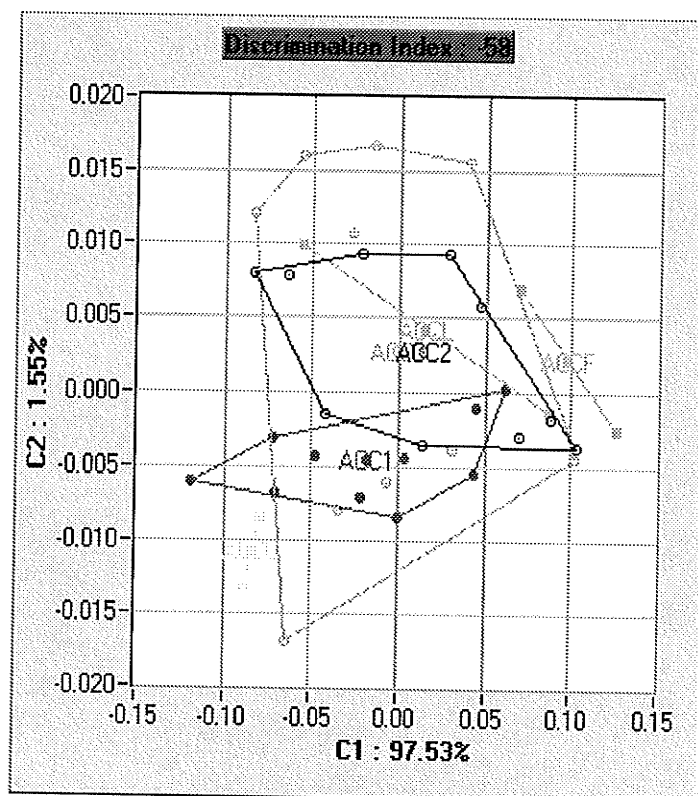


Figure 6.10. PCA map of ACC data from October 5 analyzed by distance from the odor source.

There is no useful differentiation in this data presumably due to the holding time before sample analysis – due to the breakdown of the autosampler component of the EN system.

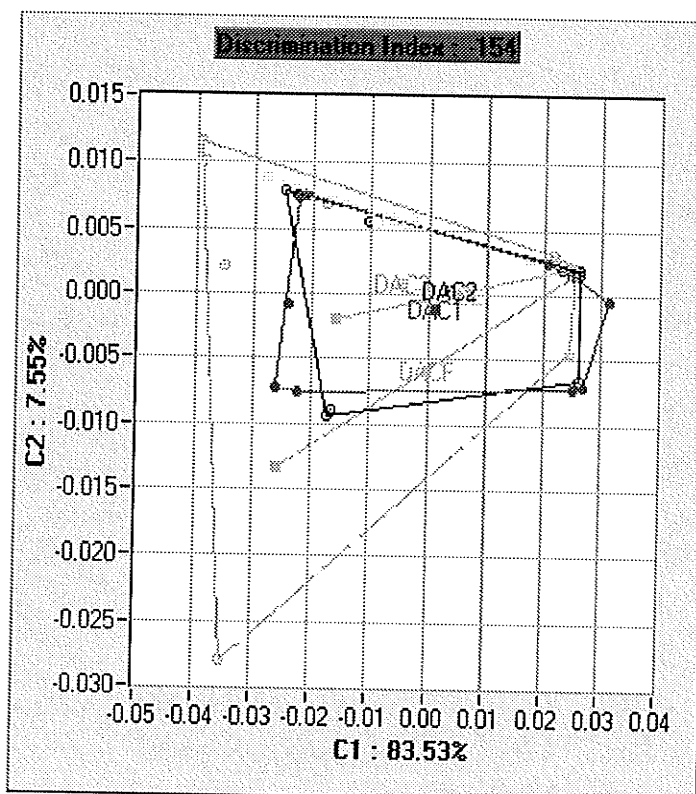
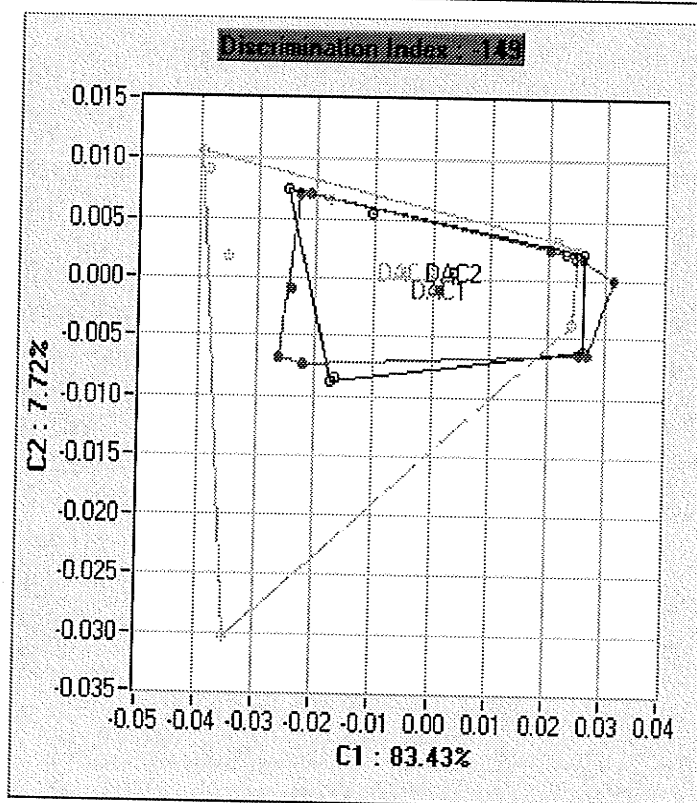


Figure 6.11 PCA map of DAC data from October 5, analyzed by distance from the odor source.

There is no useful differentiation in this data presumably due to the holding time before sample analysis – due to the breakdown of the autosampler component of the EN system.



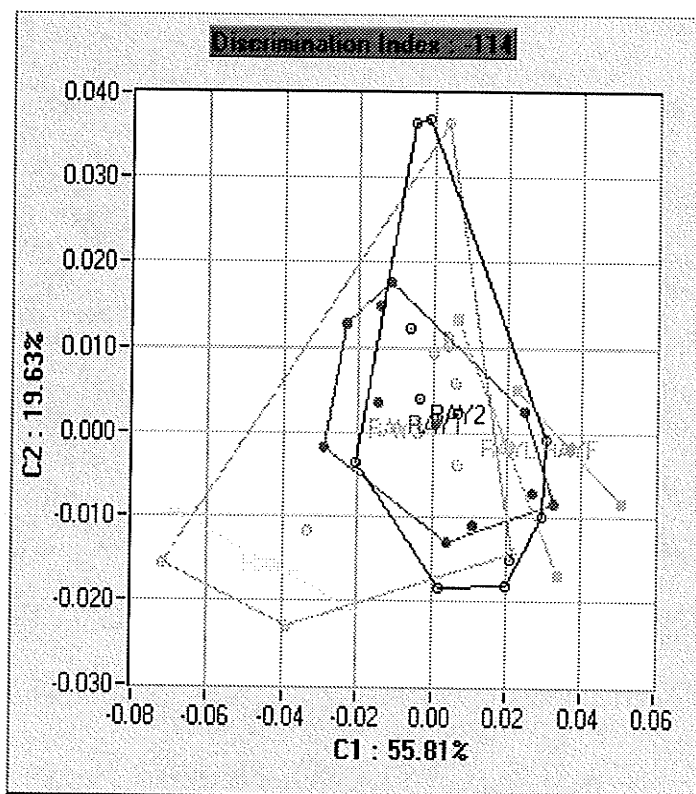
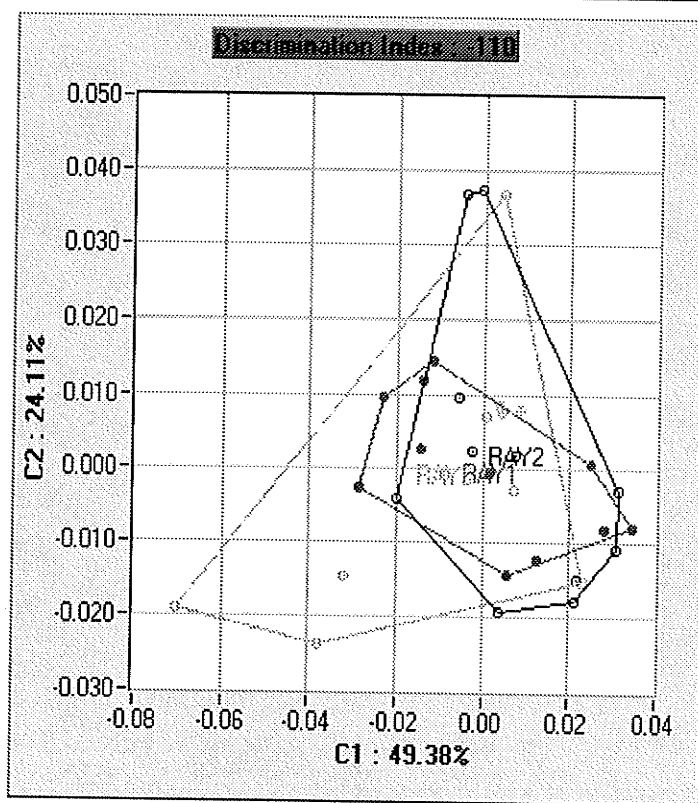


Figure 6.12 PCA map of RAY data from October 5 analyzed by distance from the odor source.

There is no useful differentiation in this data presumably due to the holding time before sample analysis – due to the breakdown of the autosampler component of the EN system.



6.3.5 Relating the Electronic Nose Analyses and the Sensory Data

The sensory scores obtained from the field panels can be used in a variety of ways that can be related to the sensor responses through linear regression (SSC) in AlphaSoft Version 8. In odor dispersion modelling, the scores were used to calculate the 10-min geometric means, which are used to calculate the models. Since no work had been done to date on relating these scores to cloth swatch analysis in this way, other methods may also be useful. Since the cloth was exposed for the complete sampling period, the individual session results were not applicable; so, all relationships are evaluated relative to the total scores for the entire sampling period. The form of the numbers that were used for the calculations are shown for each of the sampling days in Table 6.4. The numbers used could be either the geometric mean, the arithmetic mean based on all the times a reading was taken (C/A), the arithmetic mean based on the number of times an odor was perceived (C/B), or the maximum value perceived during the session.

Figures 6.13 to 6.20 each contain four SSC graphs labelled A, B, C and D which show the plot of the sensor data versus sensory data for one of the values calculated. Each indicated the overall exposure at that grid location over the entire sampling period for that fabric swatch on that date and shown in Table 6.4.

A = sensor data versus sensory data using Mean #1

B = sensor data versus sensory data using Mean #2

C = sensor data versus sensory data using maximum sensory value assigned during sampling

D = sensor data versus sensory data using Geometric Mean

These graphs were generated for each of the sampling dates for all of the swatches tested to evaluate what had happened at each time.

Table 6.6 shows the correlation coefficients for all of the correlation coefficients calculated using the linear regression or Sensory Score Correlation of the sensor signals versus

sensory scores assigned at each of the locations in the grid. The samples that showed a correlation coefficient of 0.7 or greater are highlighted in the table.

Allowing for all of the problems in sample analysis for the September 21 and October 5 sampling dates some interesting relationships could be seen in Table 6.6. The main one was the effectiveness of activated carbon cloth in retaining an odor sample, which seemed to relate to the sensory values calculated from the field data. In general, the highest correlation coefficients for sensor readings with sensory scores were with the maximum value recorded, (except for the activated carbon cloth sample on September 21). With one exception, Dacron on October 5, all of the correlation coefficient values of interest were obtained with activated carbon cloth.

These results allowed Hypothesis I to be accepted for activated carbon cloth when correlated with the maximum value for data from September 14 and rejected for all other means for activated carbon cloth on this date. Hypothesis II is rejected for spun polypropylene for all of the means on this date. The correlation coefficients for all of the other fabrics from the two other testing days, September 21 and October 5, were lower than 0.8. This may be due to the delay in electronic nose analysis of these samples due to equipment breakdown.

Table 6.6. Correlation coefficients and Figure # for each of the SSC relationships calculated for various forms of the sensory data. ^a				
Fabric Date sampled Figure #	Arithmetic Mean #1 A	Arithmetic Mean #2 B	Maximum Value C	Geometric Mean D
ACC Sept 14/03 Figure 13	0.7205	0.7539	0.8019	0.7719
PLY Sept 14/03 Figure 14	0.4081	0.4583	0.6580	0.4465
ACC Sept 21/03 Figure 15	0.7567	0.7400	0.6592	0.7369
PLY Sept 21/03 Figure 16	0.4321	0.4372	0.3574	0.4585
COT Sept 21/03 Figure 17	0.5310	0.5555	0.5705	0.5587
ACC Oct 5/03 Figure 18	0.7001	0.6622	0.7299	0.6630
DAC Oct 5/03 Figure 19	0.5482	0.6402	0.7162	0.6118
RAY Oct 5/03 Figure 20	0.4656	0.3820	0.3931	0.3744
^a Each includes the control sample (CON) taken to the field but not exposed to the ambient air. The correlation coefficients which are equal to or greater than 0.8 are highlighted.				

Figure 6.13. Sensory Score Correlation (SSC) graphs for Activated Carbon Cloth (ACC) sampled on September 14, 2003.

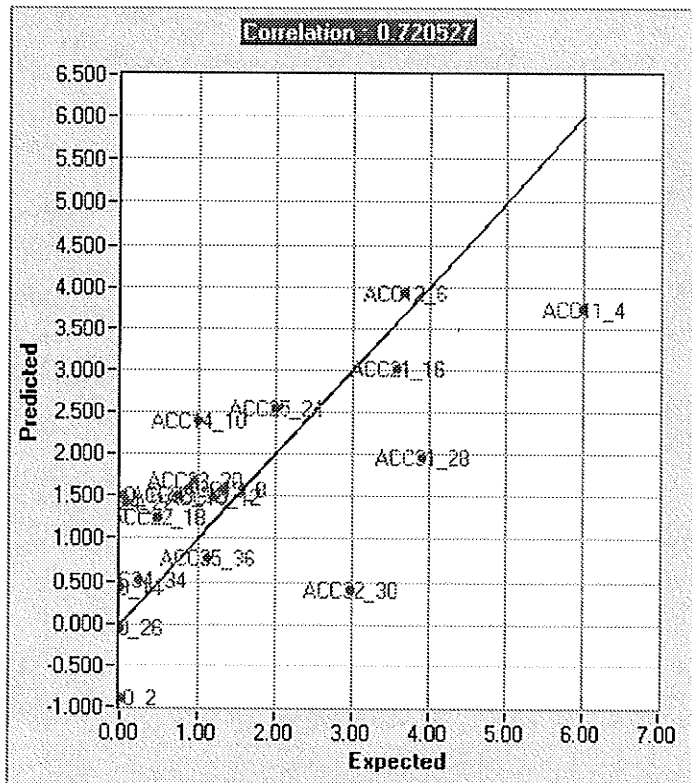


Figure 6.13A

Linear regression (SSC) for ACC versus mean #1

For September 14/03

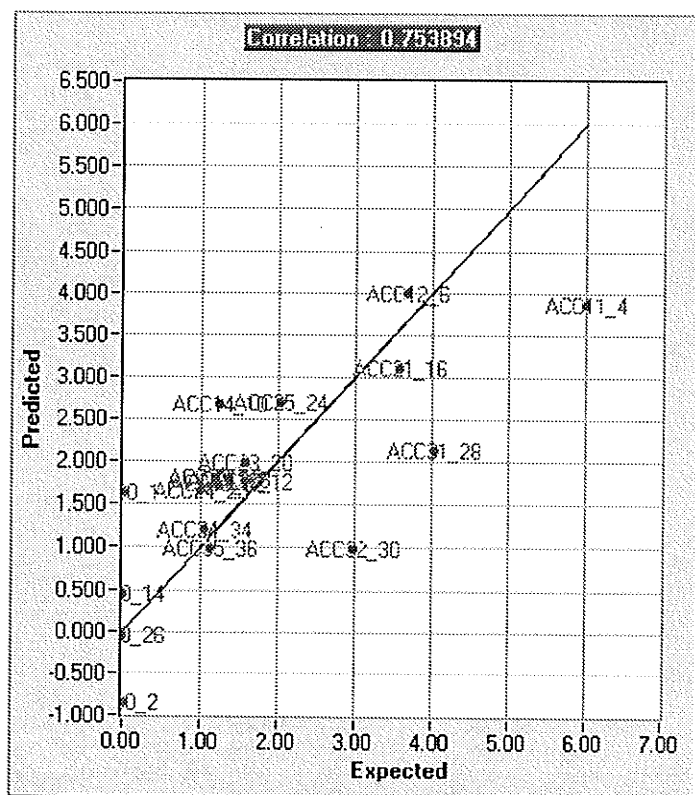


Figure 6.13B

Linear regression (SSC) for ACC versus mean #2

For September 14/03

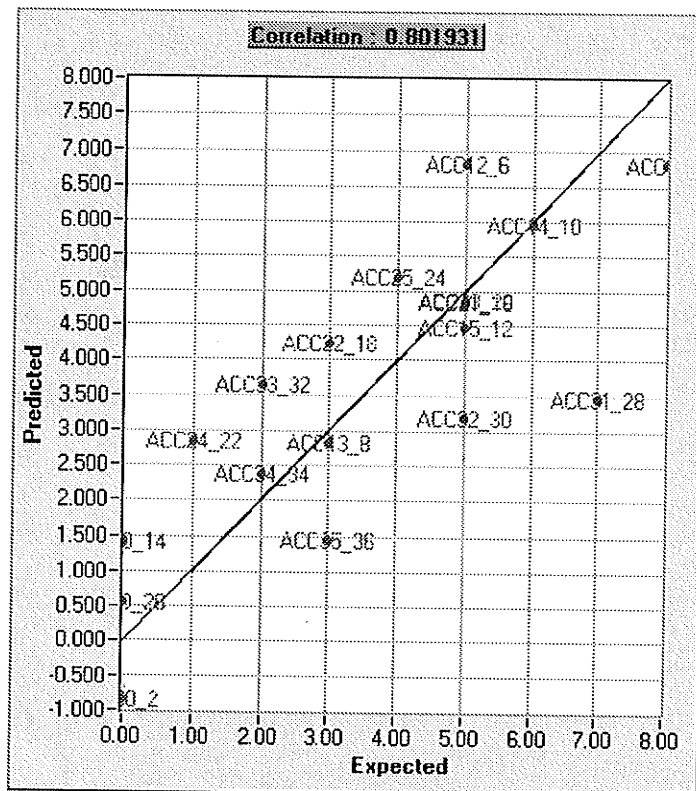


Figure 6.13C

Linear regression (SSC) for
ACC versus maximum value

For September 14/03

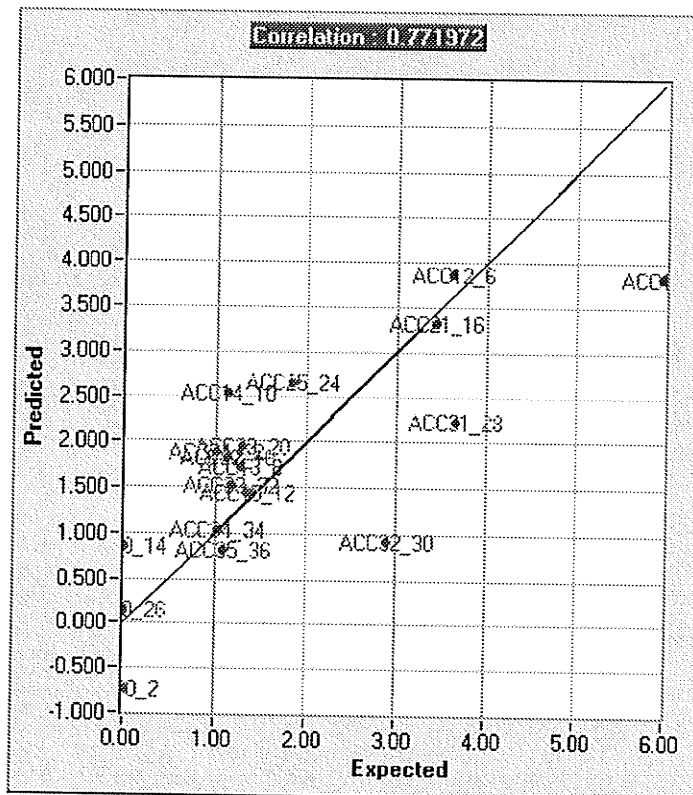


Figure 6.13D

Linear regression (SSC) for
ACC versus geometric mean

For September 14/03

Figure 6.14. Sensory Score Correlation (SSC) graphs for Spun Polypropylene (PLY) sampled on September 14, 2003.

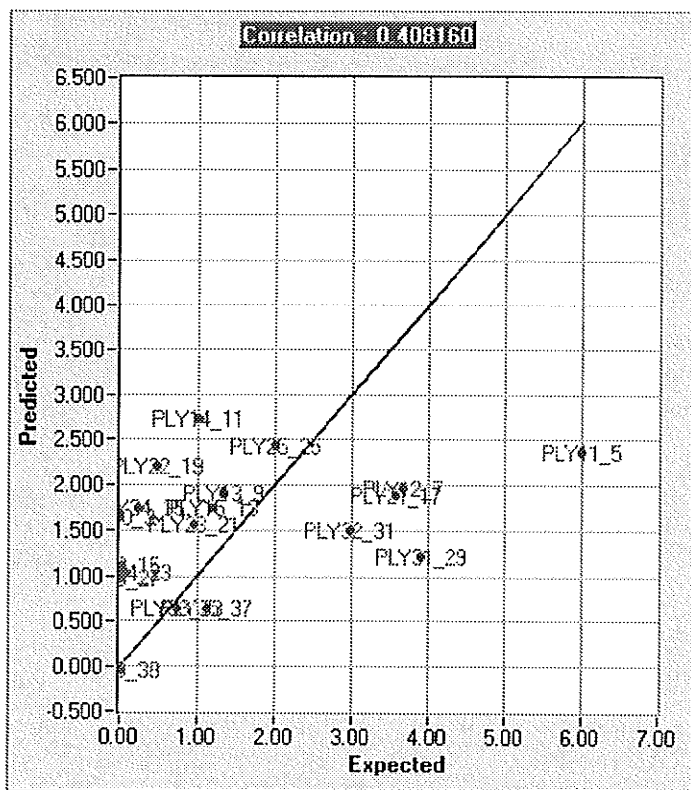


Figure 6.14A
Linear regression (SSC) for PLY
versus mean #1

For September 14/03

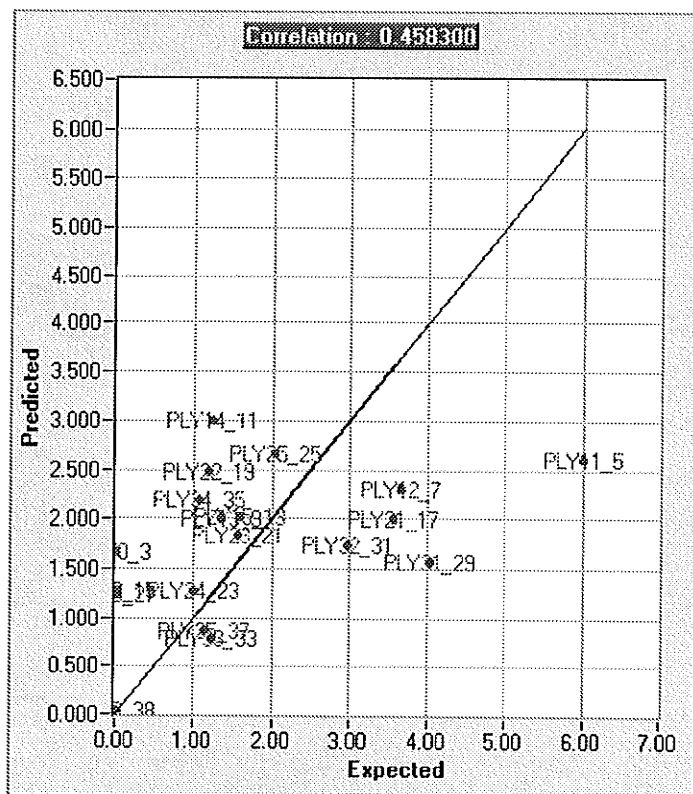


Figure 6.14B
Linear regression (SSC) for
PLY versus mean #2

For September 14/03

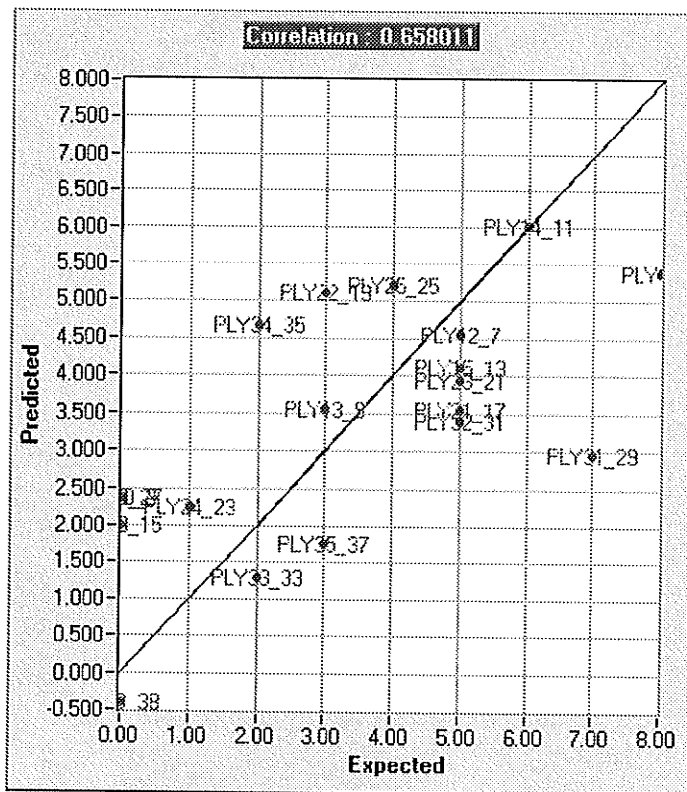


Figure 6.14C
Linear regression (SSC) for PLY
versus maximum value

For September 14/03

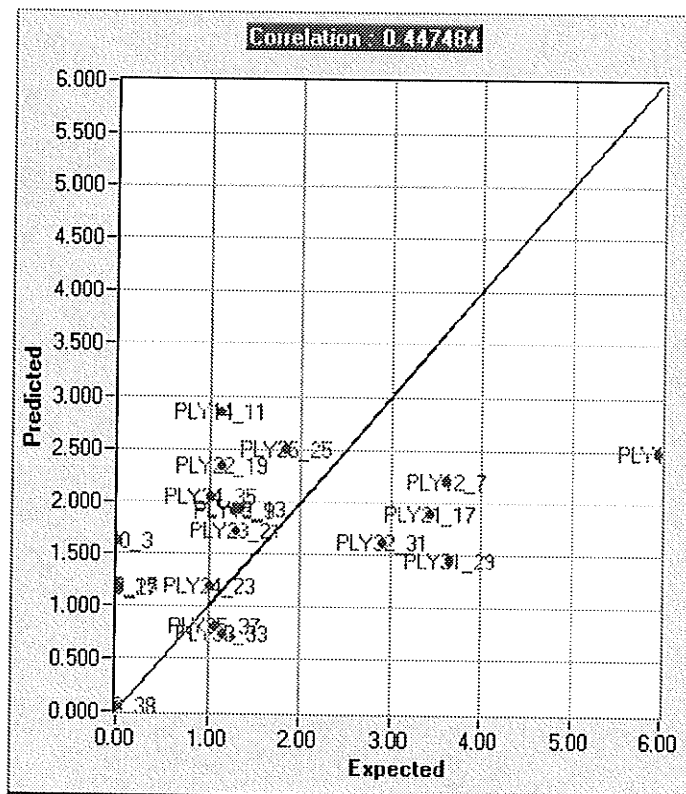


Figure 6.14D
Linear regression (SSC) for PLY
versus geometric mean

For September 14/03

Figure 6.15. Sensory Score Correlation (SSC) graphs for Activated Carbon Cloth (ACC) sampled on September 21, 2003.

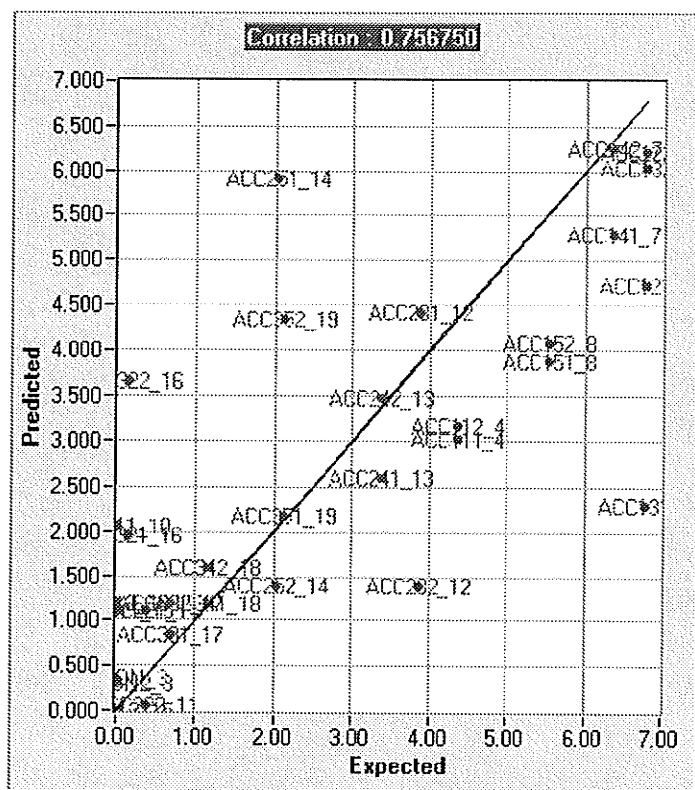


Figure 6.15A

Linear regression (SSC) for ACC versus mean #1

For September 21/03

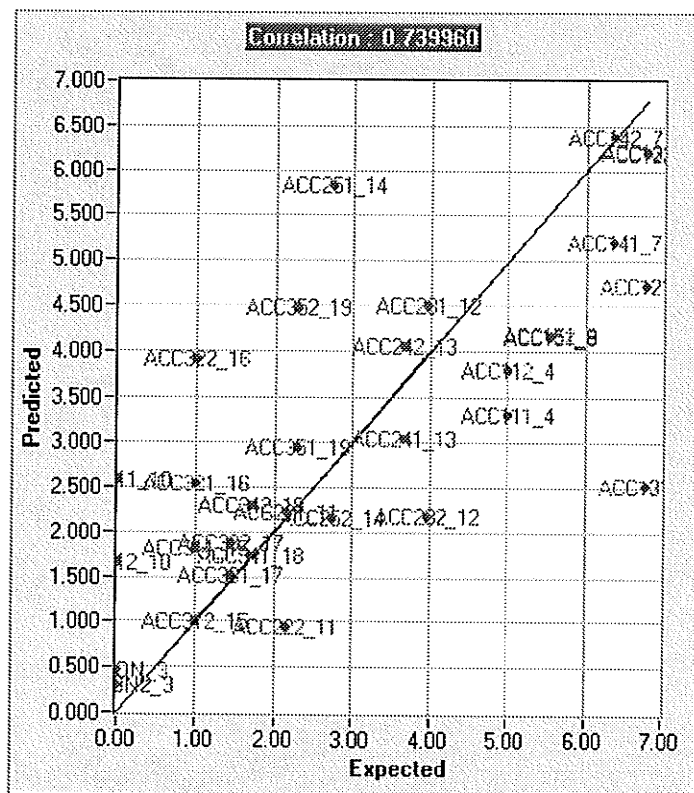


Figure 6.15B

Linear regression (SSC) for ACC versus mean #2

For September 21/03

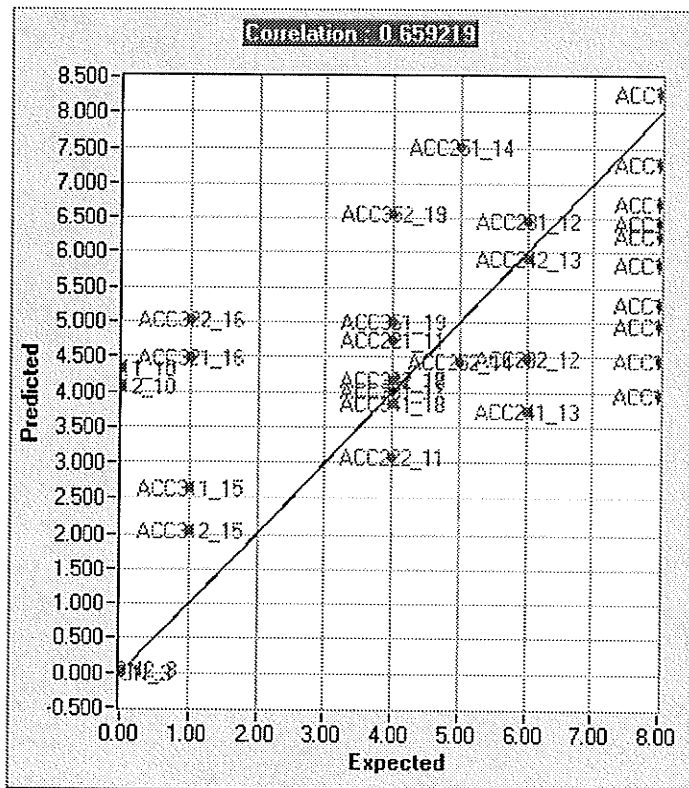


Figure 6.15C

Linear regression (SSC) for ACC
versus maximum value

For September 21/03

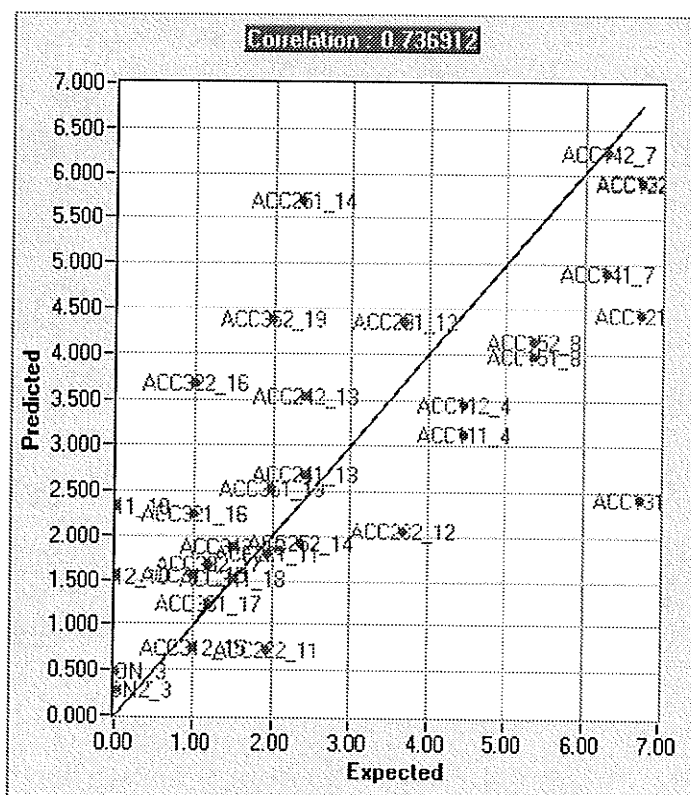


Figure 6.15D

Linear regression (SSC) for ACC
versus geometric mean

For September 21/03

Figure 6.16. Sensory Score Correlation (SSC) graphs for Spun Polypropylene (PLY) sampled on September 21, 2003.

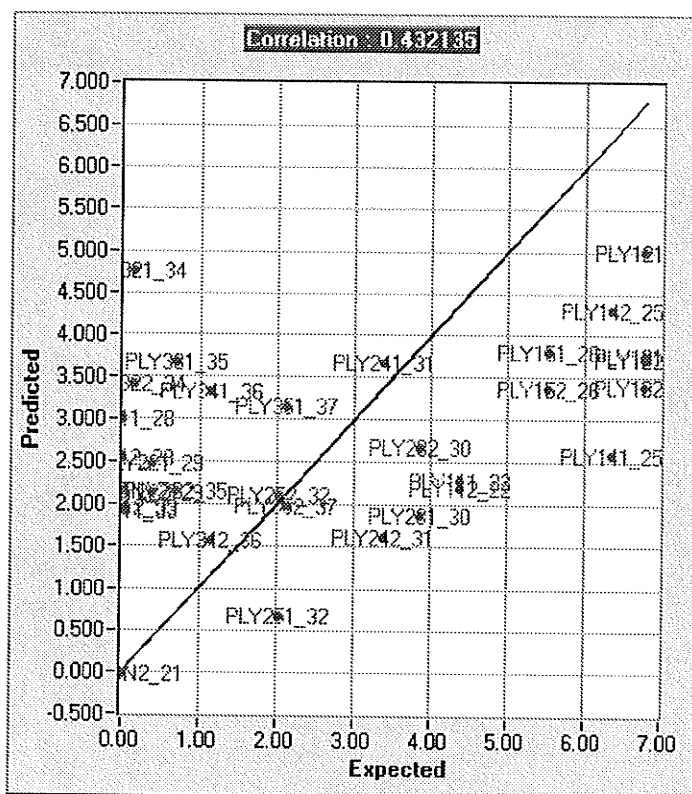


Figure 6.16A
Linear regression (SSC) for
PLY versus mean #1

For September 21/03

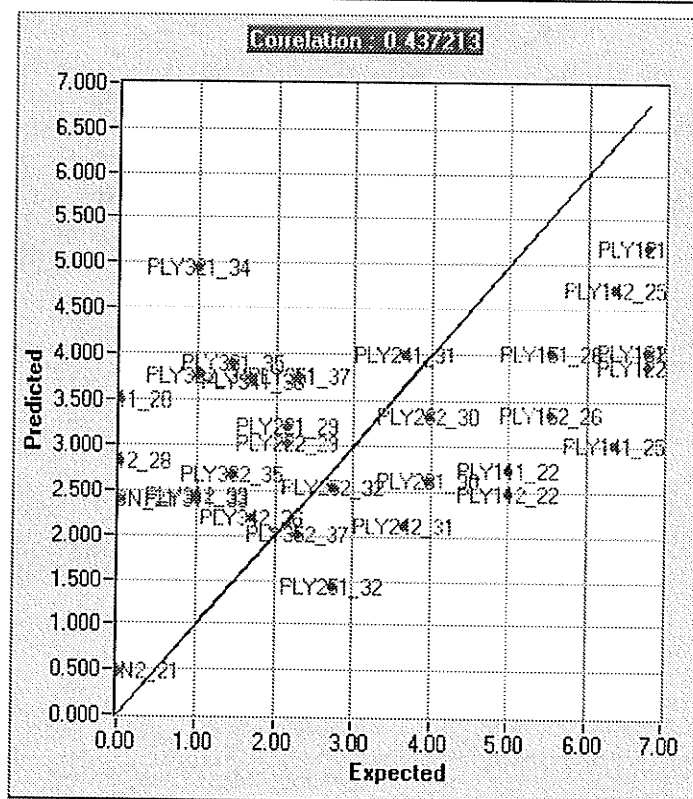


Figure 6.16B
Linear regression (SSC) for
PLY versus mean #2

For September 21/03

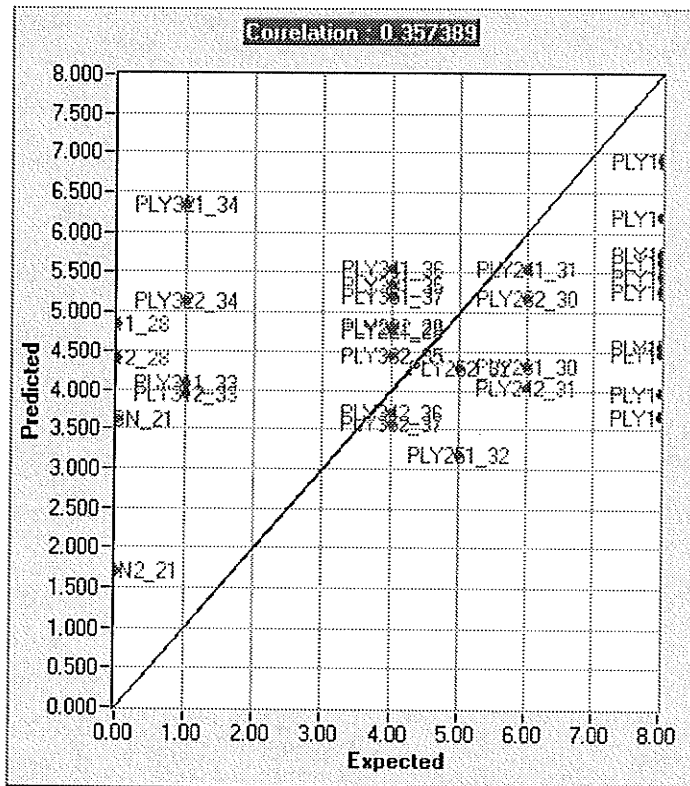


Figure 6.16C
Linear regression (SSC) for
PLY versus maximum value

For September 21/03

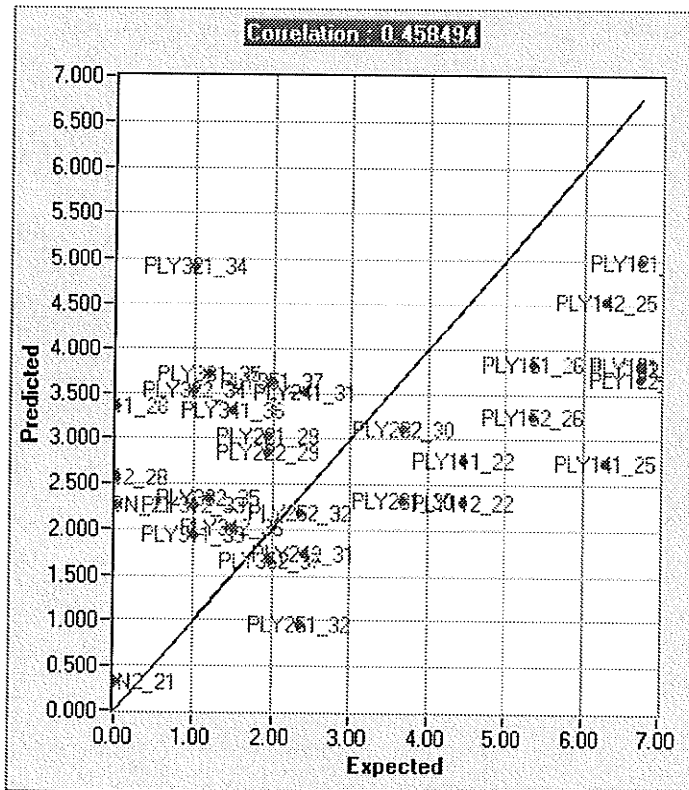


Figure 6.16D
Linear regression (SSC) for
PLY versus geometric mean

For September 21/03

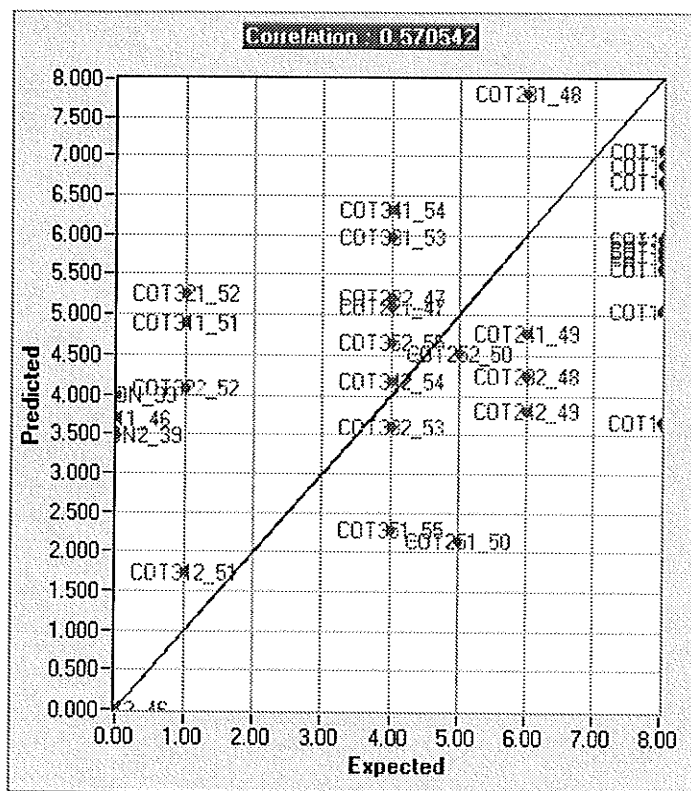


Figure 6.17C
Linear regression (SSC) for
COT versus maximum value

For September 21/03

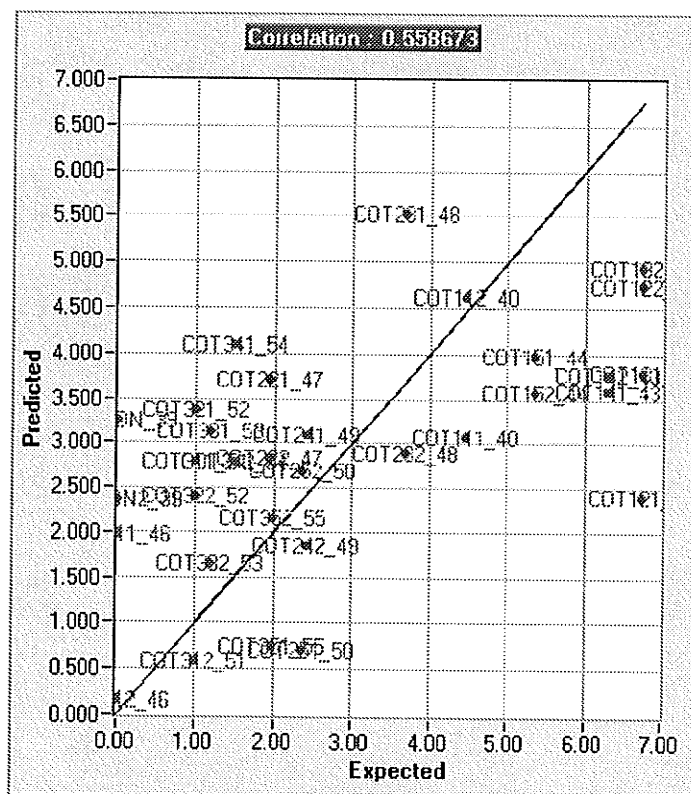


Figure 6.17D
Linear regression (SSC) for
COT versus geometric mean

For September 21/03

Correlation = 0.700123

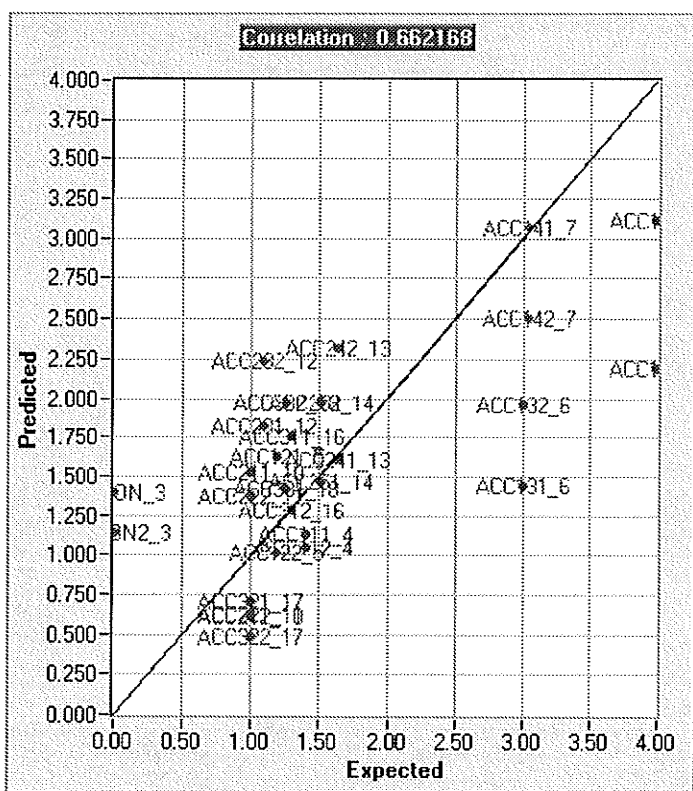
Predicted

Expected

Chemical structures plotted (from top to bottom):

- ACC#41_7
- ACC#42_7
- ACC#41_6
- ACC#42_13
- ACC#42_14
- ACC#41_13
- ACC#41_16
- ACC#42_11
- ACC#42_16
- ACC#42_5
- ACC#42_10
- ACC#42_17

For September 21/03



For September 21/03

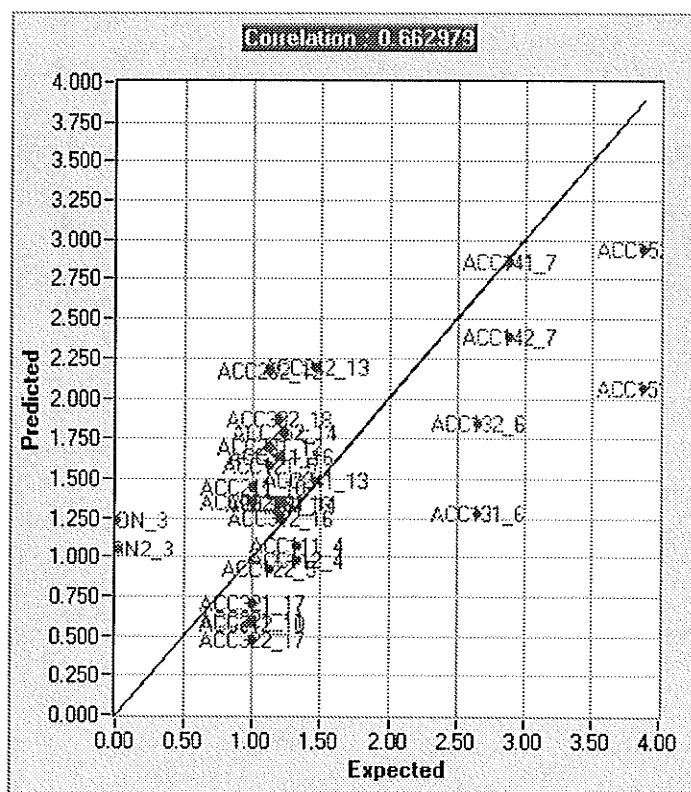
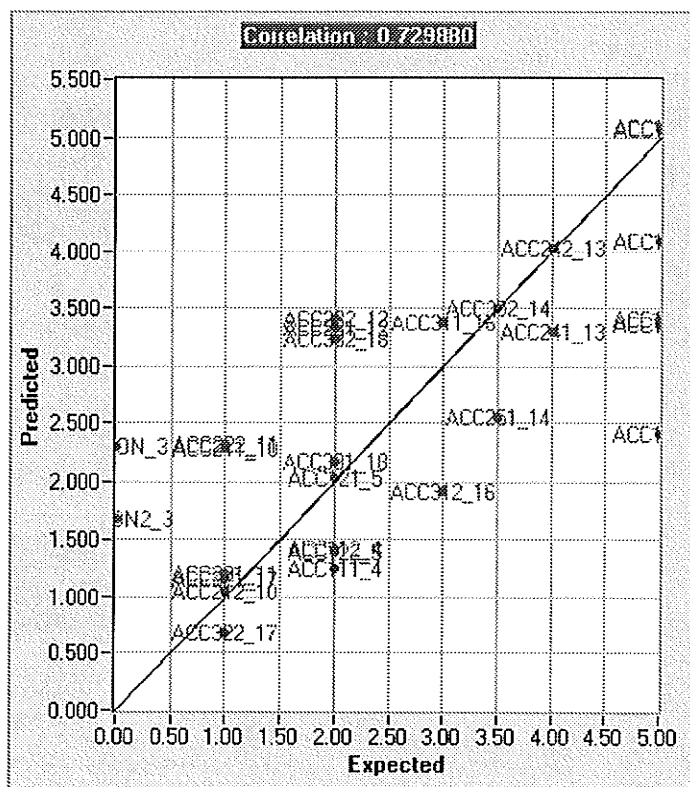


Figure 6.19. Sensory Score Correlation (SSC) graphs for Dacron type 54 (disperse dyeable) (DAC) sampled on October 5, 2003.

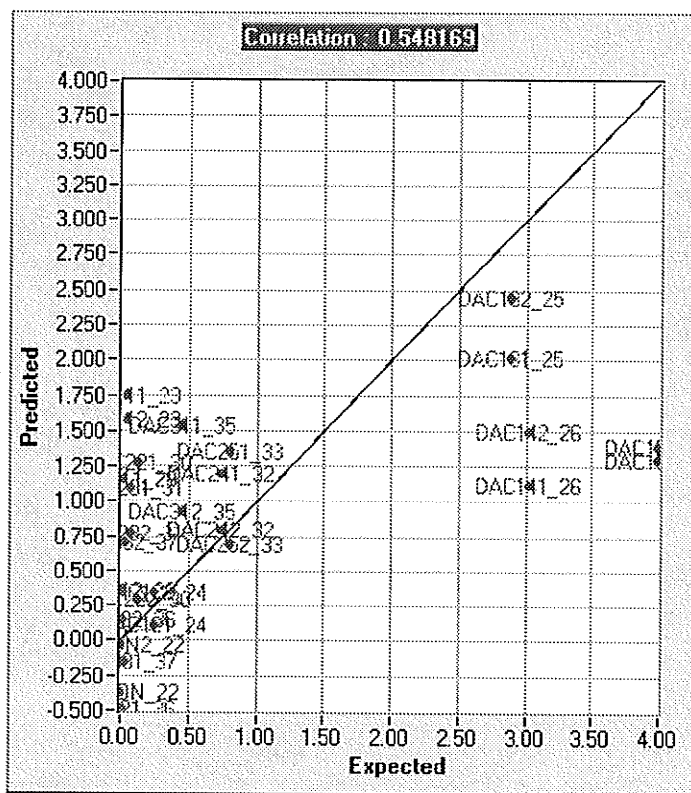


Figure 6.19A
Linear regression (SSC) for DAC
versus mean #1

For October 5/03

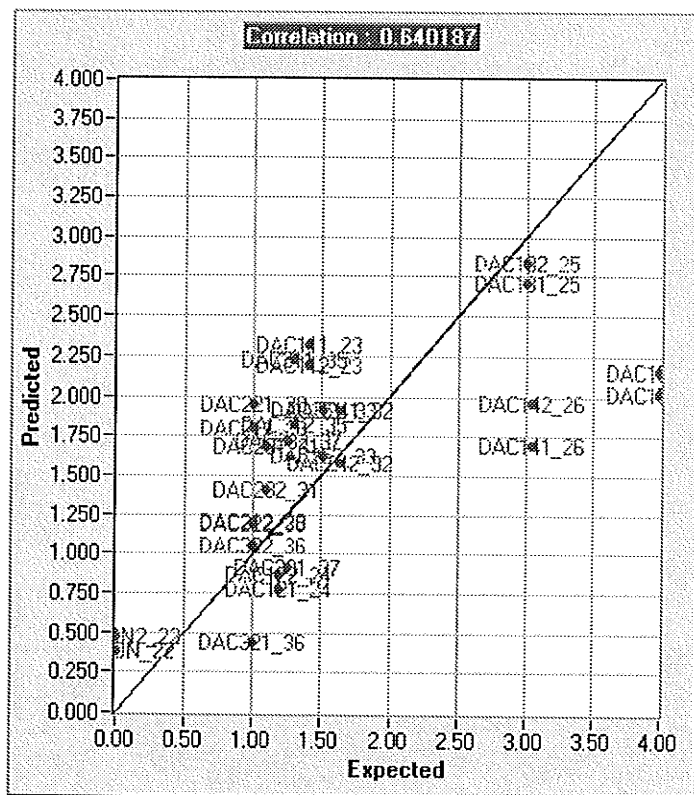


Figure 6.19B
Linear regression (SSC) for DAC
versus mean #2

For October 5/03

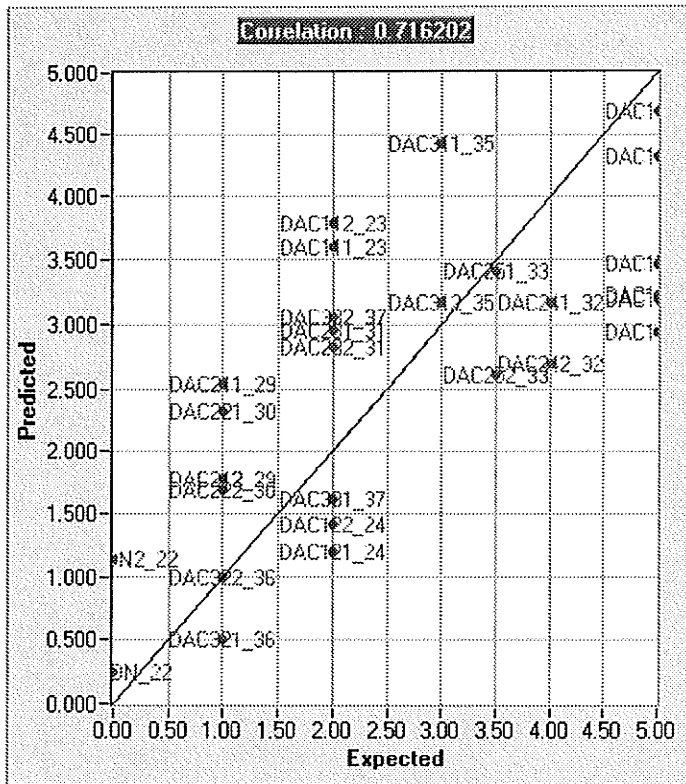


Figure 6.19C
Linear regression (SSC) for DAC
versus maximum value

For October 5/03

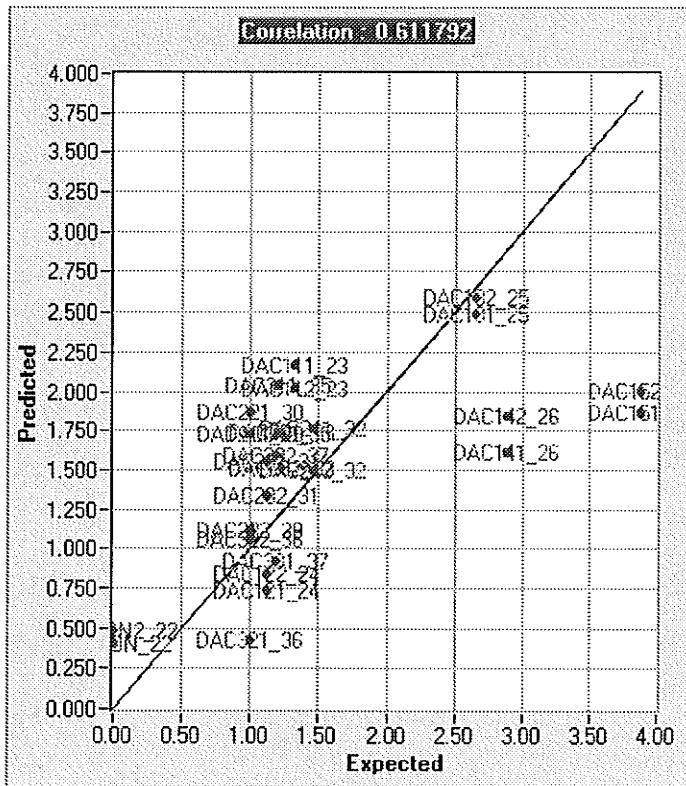
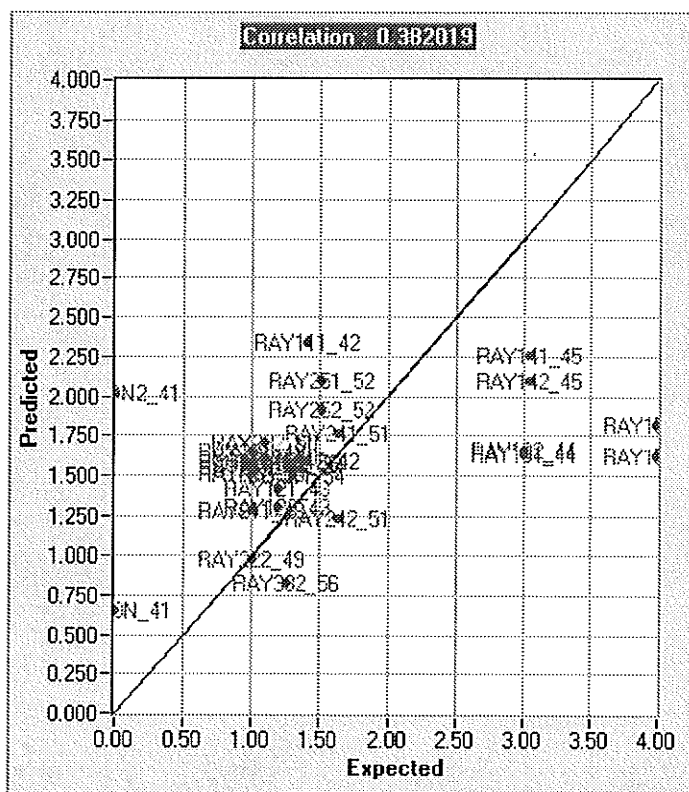


Figure 6.19D
Linear regression (SSC) for DAC
versus geometric mean

For October 5/03

[illegible]

For October 5/03



For October 5/03

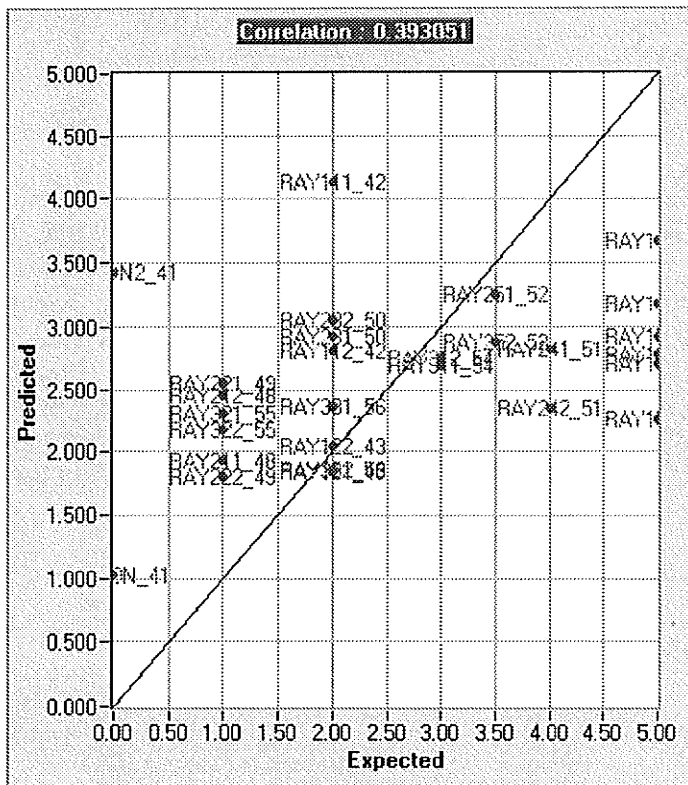


Figure 6.20C
Linear regression (SSC) for RAY
versus maximum value

For October 5/03

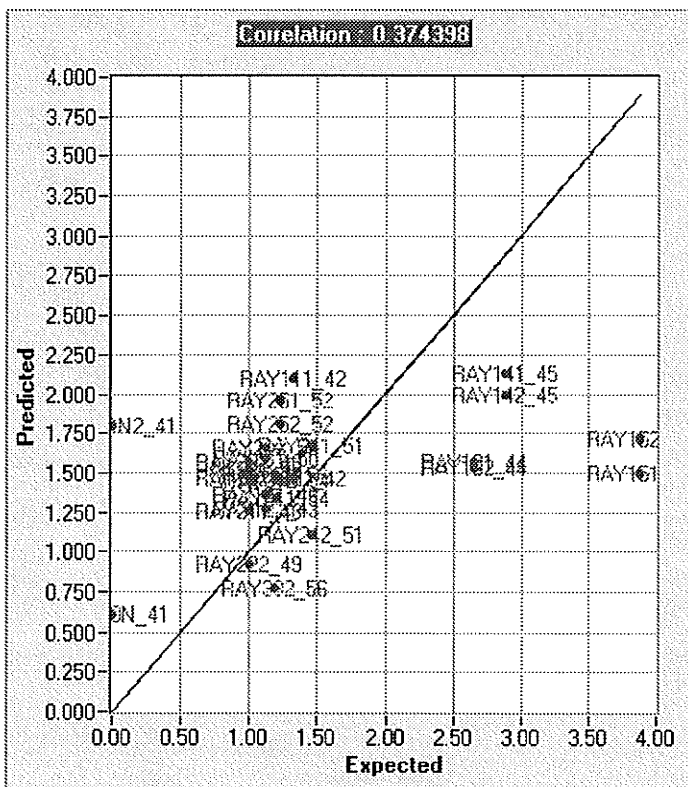


Figure 6.20D
Linear regression (SSC) for RAY
versus geometric mean

For October 5/03

6.4 Conclusions

In this work, a system for collecting cloth swatch data simultaneously with sensory data was demonstrated under field testing conditions in an odor dispersion study. The resulting swatches could be transported to the laboratory for analysis in an appropriate time frame of up to a 1-day holding time for analysis in an electronic nose system.

The results from September 14 indicated that both the activated carbon cloth and the spun polypropylene samples were able to retain an odor sample in the field and were differentiated by distance by the principal component analysis program. The comparisons of the sensory data with the sensor responses for each of these cloth swatches showed a greater correlation between the sensory values and activated carbon cloth than with spun polypropylene. This correlation would indicate that activated carbon cloth would be the fabric substrate of choice in a field-testing situation for electronic nose analysis. The spun polypropylene had performed well in Study # 2 in the laboratory sensory tests where the air speed of odor exposure was much lower and could also continue to be used in a laboratory test situation.

Limited comparisons could be made for the remaining fabrics due to the breakdown of the autosampler at the beginning of the analysis of the September 21 samples. Given that, it was still possible to make some comparisons, allowing for the deterioration of the samples. In general, activated carbon cloth showed the highest correlation coefficients when related to the sensory data, even under adverse testing conditions, reinforcing that it is likely the fabric that would be most useful for field sampling for electronic nose analysis.

Chapter 7

Study #5: Modification of the Surface Chemistry of Selected Cloth Swatches using Plasma Polymerization

7.1 Introduction

One assumption in using cloth swatches as a substrate for odor adsorption was that the surface chemistry of the sample would govern the degree to which odor is adsorbed. The previous work described the ability of fabrics with their innate surface characteristics to adsorb odor, and the ability to do this varied greatly with the specific fabric, even within one fibre type (i.e., cotton). One way to explore the influence of the surface chemistry further, was to change the nature of the fabric surface chemistry and evaluate the effects on odor uptake through the electronic nose.

The manner in which odor is adsorbed onto a textile surface was not well documented, although it may well be known in specialized testing for the manufacture of products such as scented laundry softeners. If this information exists, it was likely held as proprietary and unavailable. The change in the surface of a fabric would help to show whether it is the surface chemistry (most likely) or the surface structure that most influenced the uptake of odor.

Surface characteristics of fibres were modified commercially through the use of a process called “plasma polymerization”. This method could be used to change a hydrophilic surface (such as cotton) to being hydrophobic through treatment with fluorine (“Teflonizing®”) and a hydrophobic to hydrophilic with oxygen treatment. This method involved the exposure of the cloth to an atmosphere of ionized gas of specific composition under specific atmospheric conditions (Hwang, 2003).

In order to know that the surfaces had been changed in the “opposite direction” (i.e., hydrophilic to hydrophobic and hydrophobic to hydrophilic), the fabrics chosen were extremes of each of these with cotton (cotton flannel) being hydrophilic and polypropylene being hydrophobic. The two chosen treatments were designed to reverse the condition of each of the

fabrics, and both treatments were given to both fabrics so that they could serve as their own controls. The use of O₂ added –OH groups to the surface. It is expected that there would be some increase in roughness through etching of the surface, although this etching was kept to a minimum by controlling the exposure time to 1 min. These –OH groups would cause an increase in wettability of the fabric as well as adhesion.

The purpose of this final study was to explore modifying the surface of the fabric, to change the surface chemistry and evaluate the effect of the change on odor uptake through electronic nose testing. A second purpose was to evaluate the actual substantivity of the swine malodor through the swine odor simulant and its presence on the fabric over time. Changes in the surface chemistry may also be accompanied by a change in substantivity of the odor on the fabric. The hypotheses being tested were that plasma polymerization treatment of the fabric surfaces would change their chemical structure and will increase the substantivity of the fabric for use in odor sampling.

Two of the methods of establishing the change in the surface of the fabric were contact angle measurements (of a water droplet) and electron analysis for chemical analysis (ESCA). Contact angle measurements involved the placement of a precisely measured droplet of water onto the surface of the fabric and the immediate measurement of the angle between the droplet and the fabric surface. Another was through electron analysis for chemical analysis/X-ray photoelectron spectroscopy (ESCA/XPS) analysis of the surface for its actual chemical composition.

Ratter (1996) provided the following information on ESCA. The basic principle of the ESCA method has been described as “X-ray photons of precisely defined energy bombard the surface, electrons are emitted from the orbitals of the component atoms, electron kinetic energies are measured, their electron binding energies can be determined enabling the component atoms to be determined” (Vickerman, 1997, p.4), and as “X-rays are focused upon a specimen. The interaction of the X-rays with the atoms in the specimen caused the emission of a core level

(inner shell) electron. The energy of this electron was measure and its value provides information about the nature and environment of the atom from which it came” (Ratner, 1996, p.23).

The method measured the outermost 100 Å of a surface. Although the electron beam could penetrate deeply into a specimen, the electrons from those layers would lose their energy by collisions before they ever get to the surface; so, would not emerge from the surface. Only those at or near the surface would be emitted and gathered in the signal (Ratner, 1996). The method was readily applicable to biomaterials and hence textiles. The surface structure could vary widely from:

1. Rough, smooth or stepped
2. Composed of different chemistries (atoms and molecules)
3. Structurally or compositionally inhomogeneous in the plane of the surface
4. Inhomogeneous with depth into the specimen
5. Covered by an over-layer
6. Highly crystalline or disordered.

In other words, it would work on almost any surface (Ratner, 1996).

The advantages of the method included the speed of analysis, the high information content, the low damage potential (non-destructive method) and the lack of specimen preparation. The disadvantages of the method were that the sample must be able to be placed in a vacuum – no out-gassing of volatile components, therefore it could not be used on swine odor simulant-exposed samples, only on the base material (i.e., the fabrics altered by plasma polymerization). This problem could be avoided using a system with a cryogenic sample stage where at liquid nitrogen temperatures, samples with volatile components and wet samples could be analyzed. Other disadvantages included the possibility of sample damage if long analysis times are used, the need for an experienced operator for the equipment, and the high cost of purchasing and maintaining the equipment (Ratner, 1996).

The information that could be obtained from this method was given as “chemical composition” and “chemical structure” (Vickerman, 1997). Ratner (1996) expanded on this with the following list for biomaterials:

1. Identification of all elements (except H and He) present at concentrations of > 0.1 atomic %
2. Semi-quantitative determination of the approximate elemental surface composition ($\pm 10\%$)
3. Information about the molecular environment (oxidation state, bonding atoms, etc.)
4. Information about aromatic or unsaturated structures from shake-up transmissions
5. Identification of organic groups using derivatization reactions
6. Non-destructive elemental depth profiles 100 Å into the sample and surface heterogeneity assessment using angular-dependent ESCA studies and photoelectrons with differing escape depths
7. Lateral variations in surface composition (spatial resolution is 8 to 150 μm depending on the instrument used)
8. “Fingerprinting” of materials using valence band spectra and identification of bonding orbitals

7.1.1 Objectives and Hypotheses

This study had two objectives. The first was to use two plasma polymerization treatments to modify the surface chemistry of two selected fabrics and to evaluate the effect of these modifications on malodor adsorption using electronic nose analysis. The second was to evaluate the substantivity of selected cloth swatches (treated and untreated) exposed to swine odor and held in storage for time periods of 0, 1, 4, 8 and 16 days.

Hypothesis I: that the surface chemistry of the cotton flannel and spun polypropylene fabrics was changed to a more hydrophilic character by treatment with plasma polymerization and He/O₂ treatment as measured by contact angle and ESCA analysis for percent surface composition.

Hypothesis II: that the surface chemistry of the cotton flannel and spun polypropylene fabrics was changed to a more hydrophobic character by treatment with plasma polymerization and He/C₃F₆ treatment as measured by contact angle and ESCA analysis for percent surface composition.

Hypothesis III: that cotton flannel samples treated to be either hydrophobic or more hydrophilic in nature would adsorb, retain and release odor in a pattern similar to untreated cotton flannel as measured by the principal component analysis of electronic nose sensor responses.

Hypothesis IV: that spun polypropylene samples treated to be either hydrophilic or more hydrophobic in nature would adsorb, retain and release odor in a pattern similar to untreated cotton flannel as measured by the principal component analysis of electronic nose sensor responses.

Hypothesis V: that exposed cloth swatch samples (treated and untreated) held in storage from 1 to 16 days would show the same odor patterns as freshly prepared cloth swatch samples (Day 0) as demonstrated by electronic nose analysis with principal component analysis of the patterns and linear regression analysis of the sensor signals and storage time.

7.2 Methods and Materials

7.2.1 Plasma Polymerization

7.2.1.1 Selection and Preparation of Cloth Swatch Samples

The selection of samples was based on performance in exposure tests and on the surface chemistry, so that one was hydrophilic and the other was hydrophobic. Spun polypropylene was selected as the hydrophobic base material and cotton flannel as the hydrophilic sample. Cotton flannel was chosen because of its general use through other swatch studies and its continuity through the other studies in this work.

7.2.1.2 Plasma Polymerization Treatments

The actual exposure methods used involved 1-min exposure at normal atmospheric pressure (not under vacuum) in the research facility available at the College of Textiles, NCSU.

This process was applied to the two fabrics selected (cotton flannel and spun polypropylene). Each of the cloth samples (in the form of the circular swatches used in the cassette exposure system – 37-mm diameter) was treated with a helium/oxygen (He/O₂) gas mixture or with a He/hexafluoropropane mixture (He/C₃F₆).

Because this was a research facility, the unit had been designed for a variety of applications. The specific details of the unit had been described by Matthews (2004, personal communication) as follows:

“The atmospheric plasma facility has an active exposure area of approximately 60 x 60 cm and is powered by a 4.8 kW power supply operating in the frequency range between 5 kHz and 10 kHz. The device has an inner plasma chamber installed inside of an outer chamber. The working gas is fed into the chamber through gas flow controllers. When flowing helium or oxygenated-helium into the plasma chamber, there will always be a slight amount of air due to the fact that the chamber is not pumped down and operates at atmospheric pressure. The device is capable of batch treatment of textiles using a test cell, as well as continuous operation using the roller feed system. The PET films were in this study were exposed to helium and oxygenated-helium plasma using the test cell. The test cell is a closed geometry chamber, with little to no ventilation, in which volatiles are not continuously removed. For these experiments the operating frequency of the power supply was kept constant. The exposure time was varied between 0.5 and 5.0 minutes in 30-second intervals. Input power, operating voltage, plate separation distance, and flow rates were held constant.”

The treatments are summarized in Table 7.1. Fabric swatches were treated in lots of 10 each until a sufficient number of samples (30) were prepared for all testing. Fabrics were weighed in lots of 10 each before and after testing and any change in weight recorded and calculated as percentage change.

Table 7.1 Sample treatments using plasma polymerization			
Fabric	Fabric surface	O ₂ ^a	Fluorocarbon – C ₃ F ₆ ^b
Cotton flannel	Hydrophilic	Hydrophilic	Hydrophobic
Spun polypropylene	Hydrophobic	Hydrophilic	Hydrophobic
^a He/O ₂ , 99%/1%, National Welders, compressed O ₂ , commercial grade			
^b He/hexafluoropropane mixture, 99%/1%, compressed, pre-purified, Aldrich			

7.2.1.3 Contact Angle Measurements

Contact angle measurements were performed using a Ramé-Hart, Inc. Goniometer Model A-100 located at the College of Textiles, NCSU. Although this was an older model unit, which was operated completely manually and was subject to operator error, the results gave reliable comparative results when done by the same person or persons who have agreed on the points at which the reading was to be taken. The critical factors included the location of the baseline on a fabric that was thick and/or fuzzy, and the actual point on the droplet where the line was made tangent for the reading of the angle.

The test was done by placing a 14-μL droplet of HPLC grade water onto the surface and then siting the droplet through a horizontally mounted microscope. The baseline was established, and then the tangent angle was established and read from a protractor attached to the unit. The readings were taken on both the left and right sides of the droplet and averaged. The higher the reading the steeper the angle and the greater was the hydrophobic effect of the fabric surface. The tests were performed in an open laboratory and test conditions were ambient temperature 24.7°C and 45% relative humidity. The fabrics were not conditioned before testing.

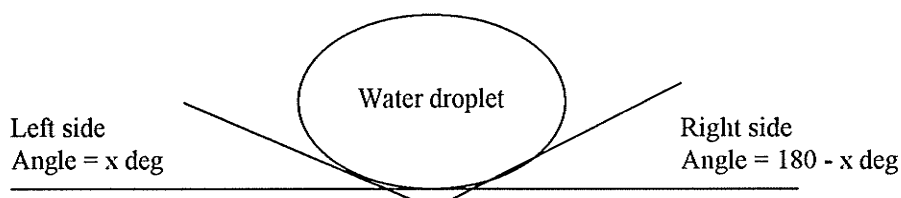


Figure 7.1. Schematic of contact angle measurements.

7.2.1.4 ESCA Testing

The samples of cotton flannel (COT, C_F, CO2) and spun polypropylene (PLY, P_F, PO2) were taken to the Quebec Biomaterials Institute, Quebec City, Canada for analysis using X-ray photoelectron spectroscopy or ESCA. The analysis was done using the procedures described in Zhang et al. (1995), whereby ESCA measurements were made using a VG ESCALAB MKII instrument (VG Scientific, East Grinstead, West Sussex, UK) with AlK α line from a standard (non-monochromatized) x-ray source perpendicular to the surface giving an analyzed area of 0.8 mm diameter. The unit was operated at 20 kV and 15 mA as source excitation. The detection angle was 45 degrees from the surface. The pressure in the sample chamber was reduced to about 10^{-8} torr and the pass energy of the analyzer was maintained at 20 or 50 eV. To prevent damage to the sample surface by X-rays, liquid nitrogen was used to cool the specimens before, and the sample holder during, the ESCA measurement. Survey scans were measured on both the internal and external surfaces of each specimen. Measurements were performed in triplicate on all samples.

7.2.1.5 Electronic Nose Analyses

The samples of cotton flannel and spun polypropylene treated with CF and O2 were given swine odor simulant exposure using the test standard conditions (2 L/min for 5 min). These samples were evaluated, along with control samples, using the program outlined in Chapter 4 and using incubation conditions of 40° C for 15 min. The results were evaluated through AlphaSoft V 8.0 for similarities or differences in the mapping patterns of the odors released from the swatches using the principal component analysis.

7.2.2 Substantivity Testing for the Storage of Samples – Substantivity of the Odor on Cloth Swatches

Substantivity is a term that was used to describe the continued presence of an odor on a substrate. Perfumers used this term in conjunction with the length of time the scent remained on the human skin. In textiles, the length of time a scent adhered to a fabric can also be referred to as substantivity, and it would be governed by the manner in which it was bonded chemically to the fabric surface. Substantivity was measured by the degree to which the original exposure level and character was maintained.

Substantivity was of interest here for both the effect it had on the field samples in Study #4 and the effect that plasma polymerization had on the treated samples. In all, nine fabrics were selected for testing of the stability of the sample (i.e., for the amount of time the sample can be stored and remain stable). The fabric swatches from Study # 4 that were selected were activated carbon cloth, rayon, and Dacron. The samples from the plasma polymerization treatments were also used (i.e., COT, CO₂, C_F, PLY, PO₂, and P_F). The cotton flannel (COT) and spun polypropylene (PLY) samples were common to both the field study and the plasma polymerization study. All of the control samples were included again in this test as the first group in this Part A of this experiment were outside the two-week stability period for the sensors.

The time frames used are shown in Table 7.2. The samples were prepared so that they could all be analyzed together over a 3-day period in the Alpha MOS Fox 3000. The electronic nose analyses were performed as described above and in Study # 2, and the data were analyzed through the principal components analysis and sensory score correlation (linear regression) subroutines in AlphaSoft Version 8.0.

Table 7. 2 Preparation and testing of cloth swatches for substantivity. Three reps of each were prepared for EN analysis.			
Test code	prep date	test date	age of sample (days)
Day 0	May 21	May 21	0
Day 1	May 20	May 21	1
Day 4	May 18	May 22	4
Day 8	May 14	May 22	8
Day 16	May 7	May 23	16

7.3 Results and Discussion

7.3.1 Plasma Polymerization

The results of the plasma polymerization treatment applied to each of the fabrics are shown in Table 7.3. The spun polyester samples showed no change in weight from either of the treatments, while the cotton showed an increase of approximately 1% for both treatments.

The surface area of the fabric swatch may be increased by the etching effect of the plasma polymerization treatment. Hwang (2003) showed that with helium/oxygen mixture, the roughness of PET films seemed to decrease at 1-min exposure and then increase up to the maximum at five-min treatment. This etching acts to increase the surface area, which was not the requirement for this study. The one-min treatment was used to prevent any great change in the surface due to etching. However, the lack of demonstrated weight change in the spun polypropylene samples may actually be due to etching of the surface, even at this treatment level. Etching could be evaluated further by scanning electron microscopy. In this case, the cotton did not appear to etch as much (if at all) as the polypropylene.

Table 7.3. Weight changes for samples prepared in plasma polymerization chamber.								
Sample		Trt. Lot #	# of swatches prepared	Wt (g)		Mean wt per swatch (g)	% change	Mean % change
				Before trt	After trt			
COT	O2	1	10	1.3359	1.3235	0.1336	0.93	1.00
		2	11	1.4771	1.4663	0.1343	0.73	
		3	9	1.195	1.179	0.1328	1.34	
	C3F6	1	10	1.3071	1.295	0.1307	0.93	0.93
		2	10	1.3253	1.3119	0.1325	1.01	
		3	11	1.4647	1.4524	0.1332	0.84	
PLY	O2	1	10	1.788	1.7866	0.1788	0.08	0.00
		2	10	1.7841	1.7857	0.1784	-0.09	
		3	10	1.8162	1.8159	0.1816	0.02	
	C3F6	1	10	1.7675	1.7651	0.1767	0.14	0.04
		2	10	1.7947	1.795	0.1795	-0.02	
		3	10	1.777	1.7768	0.1777	0.01	
		extra	7	1.261	1.2599	0.1801	0.09	

7.3.2 Contact Angle Measurements

The contact angle measurements for the samples are shown in Table 7.4. There was a clear change in the way in which the surfaces absorbed the water droplet with the cotton – untreated and He/O₂ treated – absorbing the water so quickly that no reading could be taken and the He/C₃F₆ treated cotton flannel sample showing an angle of 101.8 degrees. This change from the droplet being immediately absorbed to the droplet staying intact for a sufficient amount of time to take a reading indicates that the hydrophilic sample had become hydrophobic. In fact, the water droplet did not absorb during the approximate 2 min that the test required to complete.

The opposite occurred for the spun polypropylene. In this case the contact angle for the untreated sample was 113.8 ° and for the fluorine-treated samples it was 119.3 °, indicating that the hydrophobic surface of the PLY had been enhanced by the He/ C₃F₆ treatment. When the PLY was treated with He/O₂, the contact angle decreased to 92.7, indicating that the fabric had become somewhat more hydrophilic. During the test, these fabrics actually absorbed the water droplet after about 1 min.

Table 7.4. Results of contact angle measurements for the cloth swatches treated by plasma polymerization.				
Fabric	Treatment	Sample #	mean of 2 readings <i>degrees</i>	overall mean <i>degrees</i>
Cotton	control	1	wetted immediately no reading	0
		2	wetted immediately no reading	
		3	wetted immediately no reading	
	O2	1	wetted immediately no reading	0
		2	wetted immediately no reading	
		3	wetted immediately no reading	
	F	1	94.0	101.8
		2	112.5	
		3	99.0	
Spun Polyester	control	1	110.5	113.8
		2	109.5	
		3	121.5	
	O2	1	91.5	92.7
		2	93.5	
		3	93.0	
	F	1	122.5	119.3
		2	118.5	
		3	117.0	
Note: one of the PLY-F samples actually absorbed the droplet before a reading could be taken. Another was substituted for this sample, as it may have been operator error.				

7.3.3 ESCA Testing

The results from the ESCA analysis give the surface composition of each of the samples and allow comparisons of the effects of the different treatments. The chemical composition of each of the samples is shown in Table 7.4, and the original curves from which these were taken are shown in Appendix K. The values obtained show He/O₂ treatment of cotton flannel for 1 min significantly raised the level of oxygen on the surface from 31.89% ± 0.46% to 34.07% ± 0.51%. The same result was present in the spun polypropylene samples where the O₂ level went from

6.50% $\pm$ 0.62% to 10.73% $\pm$ 0.32%. The treatment with He/ C₃F₆ was successful in altering the surface of each of the fabrics as well. The cotton flannel had a level of 2.4% $\pm$ 0.56%. The spun polypropylene showed the same increase in fluorine on the surface, but to a much higher level. In the table, two values are shown for the means and standard deviations for the %C, %O and %F, as one of the triplicate readings was very different from the other two shown by the much higher standard deviation for each of these values in the P_F sample. Using the assumption that the means for which the standard deviations were in the same range as the others is correct, then the percentage of fluorine for the treated samples was 8.80% $\pm$ 0.14%. By way of comparison to another analysis of a polypropylene textile, in this case sutures, the composition of polypropylene found by Urban et al. (1994) using this type of analysis was C = 88.7%, O = 7.9% and other = 3.4%. This result is quite different in %C from our results, but similar for %O. The nature of the “other” components was not discussed in this paper.

Table 7.5. Elemental concentrations of the fabric surfaces from ESCA analysis. Each is the mean of three readings plus the standard deviation to indicate the consistency or variability of the treatments/readings.						
Swatch	%C		%O		%F	
	mean	std dev.	mean	std dev.	mean	std dev.
COT	68.17	0.46	31.83	0.46		
CO2	65.93	0.51	34.07	0.51		
C_F	65.97	0.72	31.63	0.49	2.40	0.56
PLY	93.50	0.62	6.50	0.62		
PO2	89.27	0.32	10.73	0.32		
P_F	74.60	5.46	16.03	4.47	9.37	0.99
	77.75 ^a	0.07 ^a	13.45 ^a	0.07 ^a	8.80 ^a	0.14 ^a
Reference: Turgeon, S. (2004) personal communication						
^a calculated from 2 readings, as one appeared to be an anomaly, based on the other results from this analysis.						

The combination of the contact angle and ESCA results showed that the surface chemistry of the treated samples was definitely altered and the hydrophilic or hydrophobic nature was reversed for each of the fabrics and Hypotheses I and II were accepted. The effects of this change were observed in the electronic nose results for laboratory exposure to the swine odor simulant.

7.3.4 Electronic Nose Analyses – Effects of Plasma Polymerization on Odor Adsorption

The results of the electronic nose testing on this part of the test are shown in Figures 7.2 and 7.3. The first question for electronic nose analysis was: did the treatment make a difference in the cloth the amount of sample that the cloth would adsorb?

The results for the three cotton flannel samples are given in Figure 7.2, without and with exposure to the swine odor simulant. As could be seen, the unexposed swatches all mapped almost on top of each other and together on the left side of the map. The exposed swatches all grouped similarly on the right side of the map. This grouping would indicate that the plasma polymerization treatment did not cause any appreciable change in the initial odor of the samples nor did it cause any appreciable change in the way in which the swine odor simulant was adsorbed onto the swatches. All of them seem to have adsorbed the odorants similarly and Hypothesis III was accepted.

Figure 7.3 shows the results for the spun polypropylene swatches – both unexposed and exposed to the swine odor simulant. In this case, samples again generally grouped on the left side of the map for the unexposed samples and the middle and right side for the exposed swatches. There were differences in initial (unexposed) odor for the three different treated swatches, which are shown as grouped but mapped separately on the left side of the map. The exposed swatches show two groupings, with the untreated spun polypropylene mapped separately from the two treated swatches. Both the PO2 and P_F mapped together and farther to the right side of the map than the PLY sample. This difference would indicate that these two samples both adsorbed more of the odorant mixture than did the untreated exposed PLY sample and that Hypothesis IV was rejected. This difference might be an effect of the plasma polymerization in general, as there appeared to be no difference in the level of adsorption. The plasma polymerization treatment did cause some etching of the fibre surface – even though the 1-min treatment time was used to minimize this effect as much as possible. The increased adsorption might be due to an increase in

the actual surface area of the fibres themselves and not an effect of either the hydrophilic or hydrophobic nature of the samples. This effect could be explored further through scanning electron microscopy of the samples, which would be possible at a future date.

In considering these electronic nose results relative to the weight changes in the fabrics on treatment shown in Table 7.3, the polypropylene did not appear to show any weight gain, while the cotton showed an increase of approximately 1% for both the treatments. If this difference was due to the presence of etching in the polypropylene, while little or none occurred with the cotton, then there would have been an increase in surface area for the polypropylene and not for the cotton. It would follow that the lack of difference in the signal for the three treated cotton samples was related to the lack of change in the surface area of the cotton.

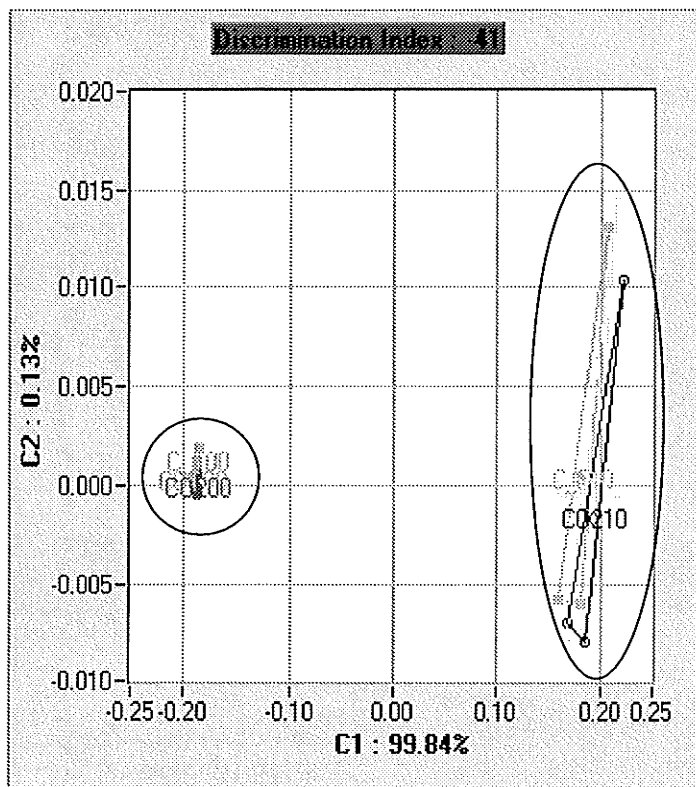


Figure 7.2 Effects of plasma polymerization on SOS adsorption for all cotton flannel samples.

PCA map of cotton flannel – with the untreated flannel (COT00), O₂-treated (CO200) and C₃F₆-treated (C_F00) shown in one group on the left and the treated versions – COT10, CO210, C_F10 – shown in another group on the right. This grouping of the unexposed and exposed swatches to the SOS – would indicate that the initial odor of the cotton flannel fabrics was unchanged by the He/O_s treatment. Also, the grouping at the right shows that all of the three cotton samples appeared to adsorb the SOS in the same manner.

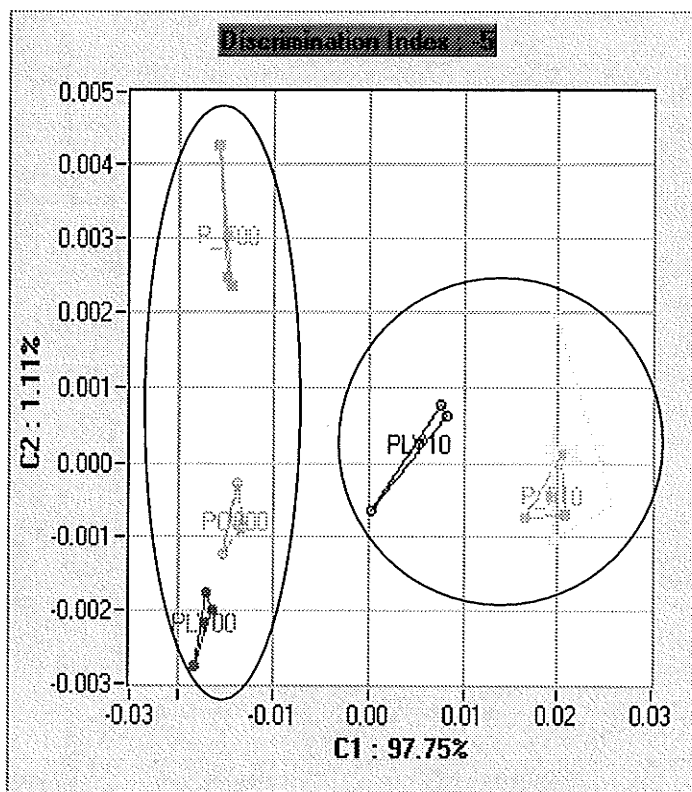


Figure 7.3 Effects of plasma polymerization on SOS adsorption for all spun polypropylene samples.

PCA map of spun polypropylene – with the untreated fabrics (PLY00), O₂-treated (PO200) and C₃F₆-treated (P_F00) shown on the left side of the map and the treated versions – PLY10, PO210, P_F10 – shown on the right side of the map – as for the cotton flannel. However, in this case the PLY changed in its base odor for the untreated swatches, shown by the separation of the samples on the PCA map. The two treated samples mapped together, even though their surfaces should have opposite characteristics, they were able to adsorb the odorants similarly. This may be due to the effects of etching during treatment increasing the surface area of the fibres.

One might expect from the above that porosity or “the proportion of void spaces or pores within the boundaries of a solid material compared to its total volume” (Guidoin et al., 1987, p. 68) would change. The greater the porosity, the larger the surface area that would be available to an odorant. However, as was seen in Chapter 4, porosity was not a good predictor of odor uptake in the cloth swatches tested.

Liu et al. (2004) discussed a study in which electron microscopy and x-ray microanalysis were used to study the distribution of an odorant (cis-3-hexenyl salicylate), which was tagged with osmium tetroxide. Three fabrics – cotton print cloth, #400 and Dacron type 54, #777 from Testfabrics, Inc., and lyocell (Tencel® chambray) – were exposed to an aliquot of the test odorant followed by exposure to osmium tetroxide vapor for several hours. Microscopic analysis showed that the odorant was distributed differently on the different fibres and was correlated strongly with the chemical structure, roughness and both pore and capillary structure of the textiles. They found that cotton was a rough and irregular collapsed tube and had both micropores large enough for the odor chemical to penetrate and interfibrillar spaces. The odorant was found through “the whole cotton fiber cross section with higher concentrations in lumen and crenulations”. In their Lyocell sample, which is the same composition as cotton but has no lumen, is round and has a microfibrillar structure with 3 phases (“crystalline, larger air-filled voids and smaller-defect regions”). The odorant “distributed evenly in the surface and cross section”. Dacron (or polyester) is formed from polyethylene terephthalate, melt-spun, and with very few or no voids. The odorant was found at a few spots on the fiber surface and in interfiber spaces of closely packed fibers”.

7.3.5 Stability or Substantivity Testing

The purpose of this series of samples was to examine the effects of holding samples before testing on the final results, referred to as sample stability or substantivity relative to each of the cloth substrates used. One question to be answered was: does changing the surface

chemistry of the surface of a hydrophilic fabric and a hydrophobic fabric change the stability of odor samples taken using the fabrics?

The fabric samples are shown in Table 7.6 along with the abbreviations used for electronic nose analysis coding and the treatment conditions used for testing the samples. The correlation coefficients (r) resulting from the SSC graphing of the sensor scores versus time in storage are also given.

Table 7.6 Fabric samples and treatments used for substantivity testing with the electronic nose and the correlations of EN readings with time for each of the samples.			
Abbreviation for EN analyses	Identity of sample	Treatment days	Correlation Coefficient from SSC
COT	Cotton flannel	All samples treated with 10 L exposure to swine odor simulant (2 L / min for 5 min) and held in vials at room temperature in darkened storage (box) – to be as for actual sample testing conditions.	0.9425
CO2	Cotton flannel treated with C ₃ F ₆		0.9603
C_F	Cotton flannel treated with O ₂		0.9411
PLY	Spun polypropylene		0.8988
PO2	Spun polypropylene treated with C ₃ F ₆		0.9084
P_F	Spun polypropylene treated with O ₂		0.9728
DAC	Dacron type 42		0.8843
RAY	Rayon		0.9504
ACC	Activated carbon cloth		0.9762

The results of the electronic nose analyses, which are given in Figures 7.4 to 7.12, showed the effects of storage time on each of the cloth swatches tested. Each set of 2 PCA maps and one graph of SSC correlation for the sensor readings versus time related the reading to the storage time the swatches were held before sampling as shown in Table 7.2. All of these samples were analyzed using all of the sensors for this work, sensor optimization was not used in this analysis.

As can be seen from the linear regression (SSC) graphs and the correlation coefficients in Table 7.5 resulting from them, all of the samples showed a definite association of change in signal, presumably a decrease in detected odor intensity with time. It is interesting to compare these correlation coefficients with the PCA maps of the same data. This pattern was not as clear

when looking at the samples in the PCA maps in Figures 7.4 to 7.12. At this point in time, there was no way to correlate the intensity of the swine odor simulant with the signals; so, there was no estimate of how great the degradation of odor was over the storage period. The change in signal with time resulted in Hypothesis V being rejected.

Table 7.7 shows the general nature of the surface chemistry of each of the samples tested, supported by the results from the contact angle measurements on each of the control and treated fabrics. The information on the remaining fabrics was taken from Gohl & Vilinsky (1983). The general observations from each of the principal component analysis maps for that fabric was also included in this table. When the general pattern of responses is examined, there appears to be one format for the hydrophilic swatches and another for the hydrophobic samples. The hydrophobic samples appear to separate in a pattern that related to the time in storage. This pattern does not appear to happen as readily for the hydrophilic samples, which, in general, all appeared to map together. There may, indeed, be a difference in the way in which the samples “held on” to the odorants that were adsorbed onto the surface based on their chemistry.

Table 7.7. Summary of the surface chemistry of the samples and the results from the PCA maps for each fabric type for all of the storage times.			
Fabric code	Fabric type	*Chemical nature of the fabric surface Hydrophilic = “+” Hydrophobic = “-”	Results from PCA maps of samples held in storage before testing
COT	Cellulose	“+”	All exposed samples (with the exception of one outlier) appear to map generally together.
CO2	Cellulose + O ₂	“+”	All exposed samples (with the exception of one outlier) appear to map generally together.
C_F	Cellulose + C ₃ F ₆	“-”	There appears to be a pattern of separation between the stored exposed samples.
PLY	Synthetic	“-”	There appears to be a pattern of separation forming between the stored exposed samples.
PO2	Synthetic + O ₂	“+”	All exposed samples appear to map generally together – with the exception of the sample stored 16 days, which

			maps separately.
P_F	Synthetic + C ₃ F ₆	“_”	There appears to be a pattern of separation forming between the stored exposed samples.
DAC	Synthetic	“_”	There appears to be a pattern of separation forming between the stored exposed samples. This seems to fall in a sequence from the freshest to the longest stored sample.
RAY	Cellulose (modified) Synthetic	“+”	All exposed samples (with the exception of one outlier) appear to map generally together.
ACC	Cellulose (modified) Synthetic (rayon is the base material from which this ACC is made).	“+”	There appears to be a pattern of separation forming between the stored exposed samples. This seems to fall in a sequence from the freshest to the longest stored sample.
*Note: This information is taken from Gohl & Vilinsky (1983) pp. 210-211 for Dacron and rayon.			

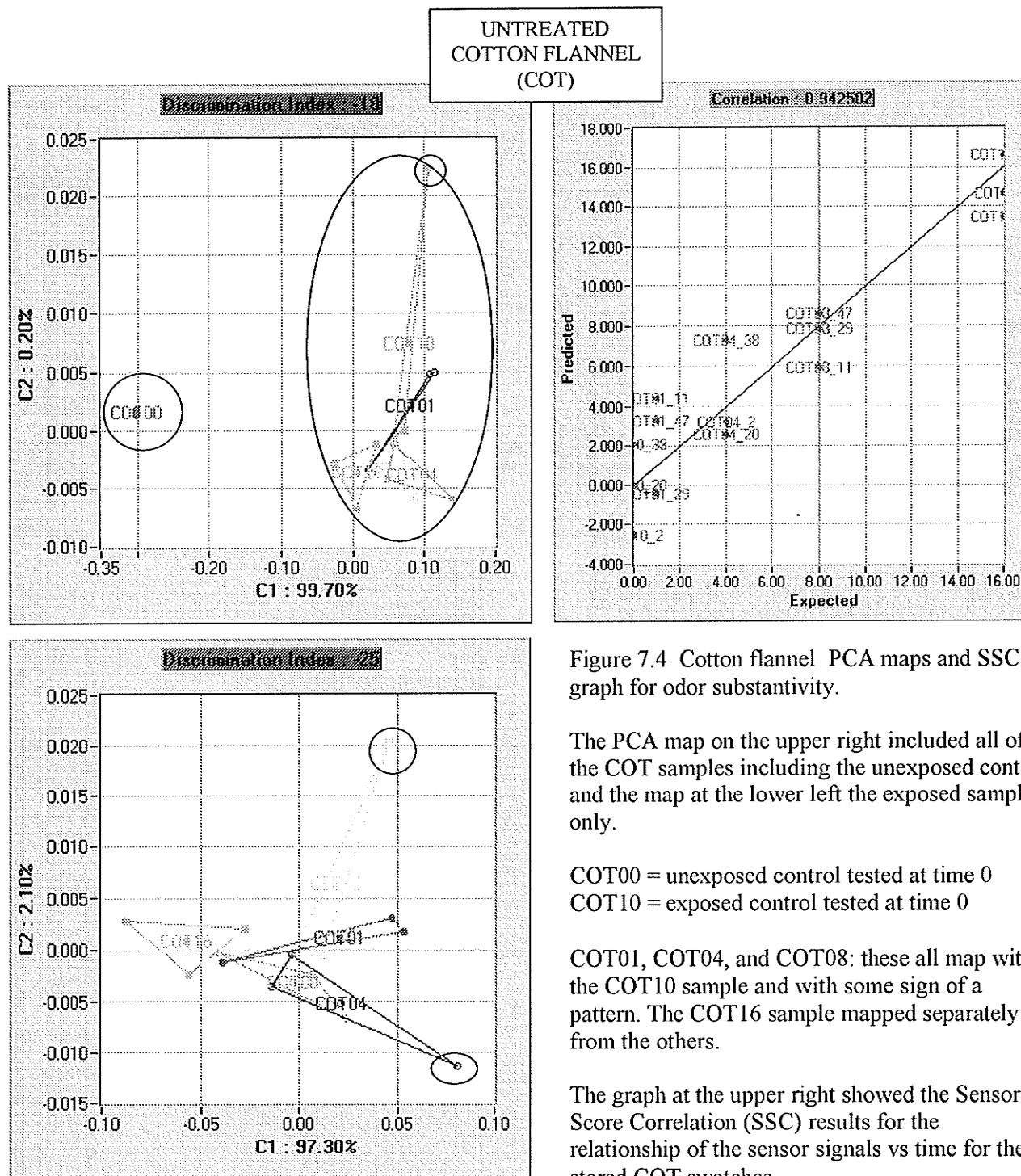


Figure 7.4 Cotton flannel PCA maps and SSC graph for odor substantivity.

The PCA map on the upper right included all of the COT samples including the unexposed control and the map at the lower left the exposed samples only.

COT00 = unexposed control tested at time 0
COT10 = exposed control tested at time 0

COT01, COT04, and COT08: these all map with the COT10 sample and with some sign of a pattern. The COT16 sample mapped separately from the others.

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored COT swatches.

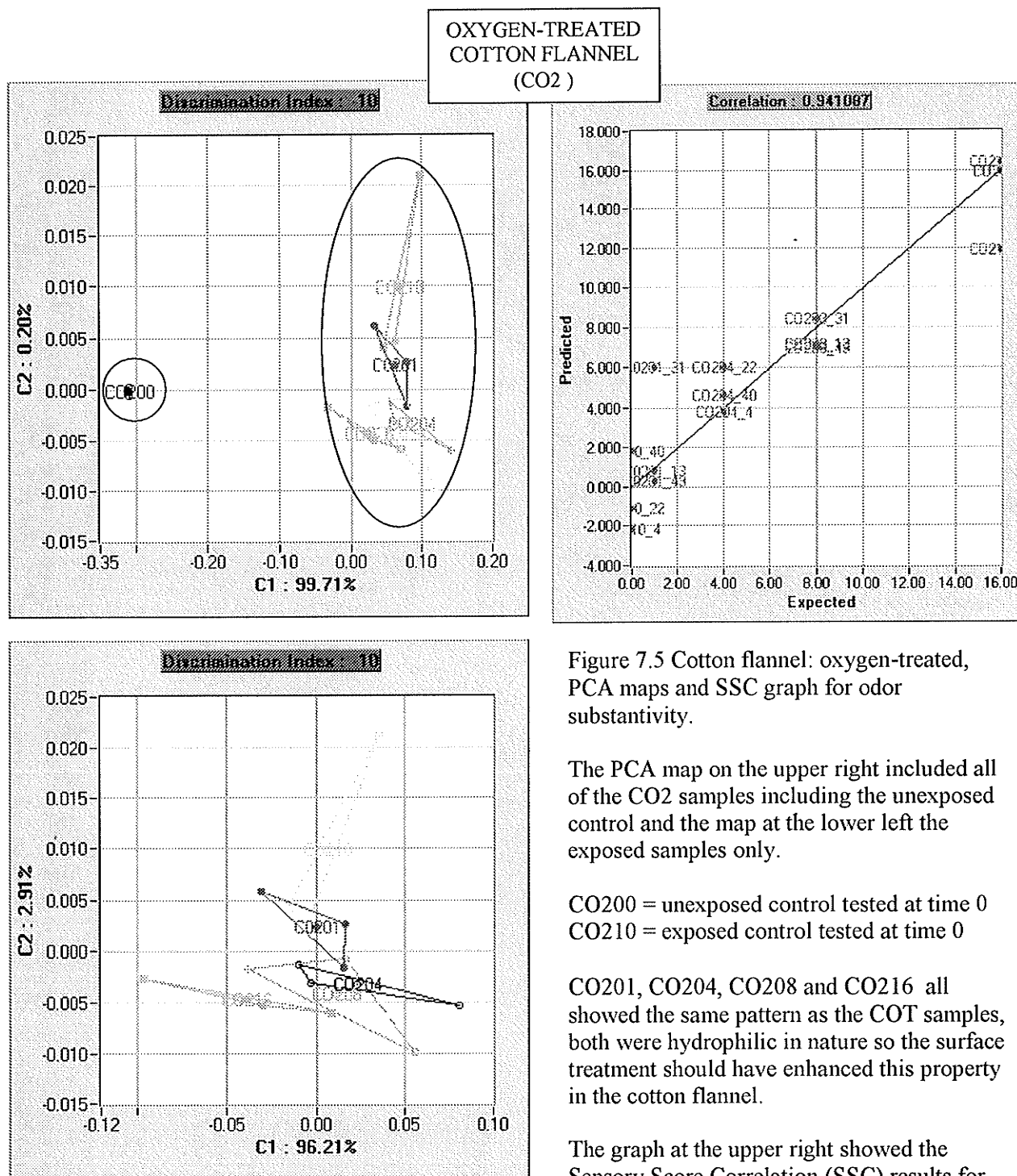


Figure 7.5 Cotton flannel: oxygen-treated, PCA maps and SSC graph for odor substantivity.

The PCA map on the upper right included all of the CO₂ samples including the unexposed control and the map at the lower left the exposed samples only.

CO₂00 = unexposed control tested at time 0
CO₂10 = exposed control tested at time 0

CO₂01, CO₂04, CO₂08 and CO₂16 all showed the same pattern as the COT samples, both were hydrophilic in nature so the surface treatment should have enhanced this property in the cotton flannel.

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored CO₂ swatches.

FLUORINE-TREATED
COTTON FLANNEL
(C_F)

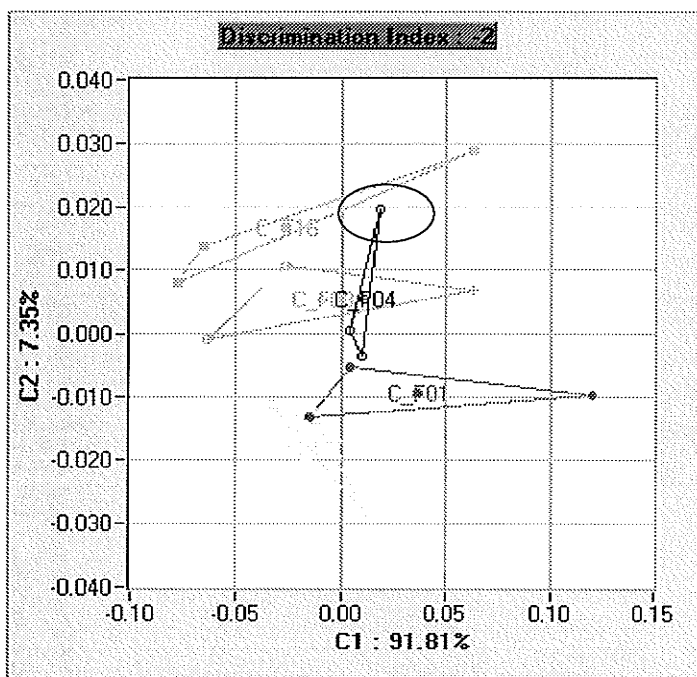
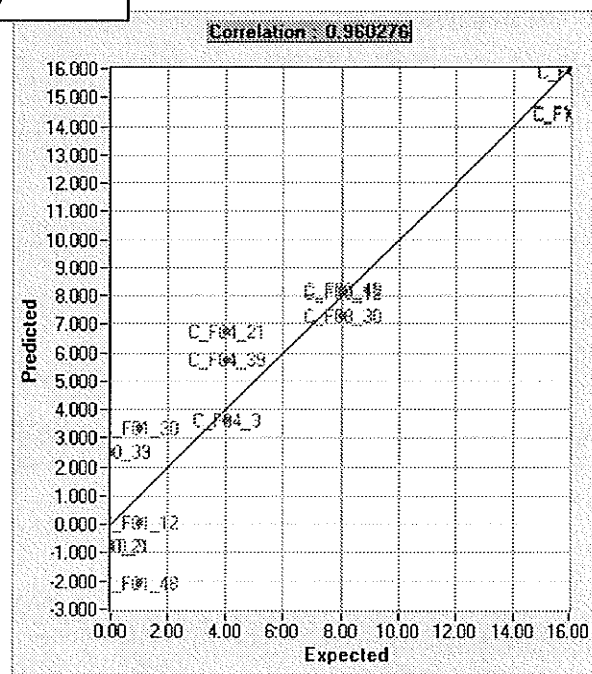
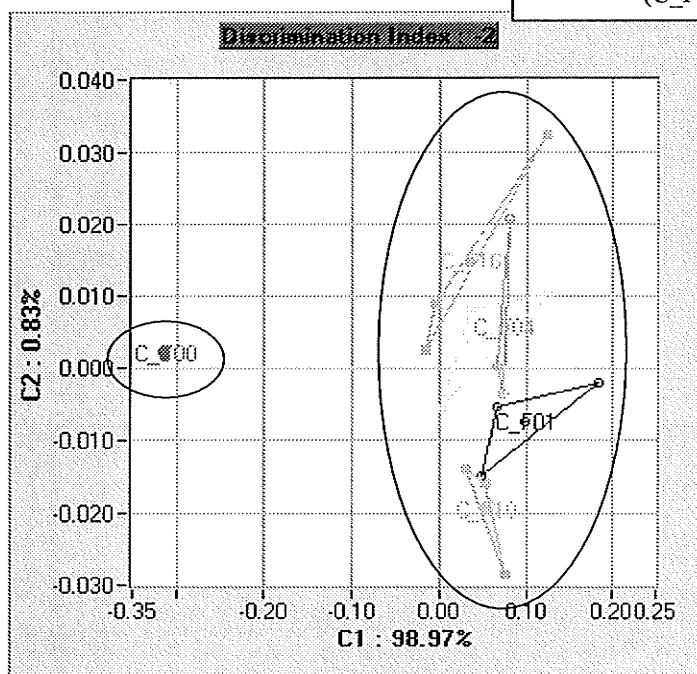


Figure 7.6 C₃F₆ treated cotton flannel: PCA maps and SSC graph for odor substantivity.

The PCA map on the upper right included all of the C_F samples including the unexposed control and the map at the lower left the exposed samples only.

C_F00 = unexposed control tested at time 0
C_F10 = exposed control tested at time 0

C_F01, C_F04, C_F08 and C_F16 all appeared to map in a pattern, generally separate from one another, with the exception of one outlier on the C_F04 sample

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored C_F swatches.

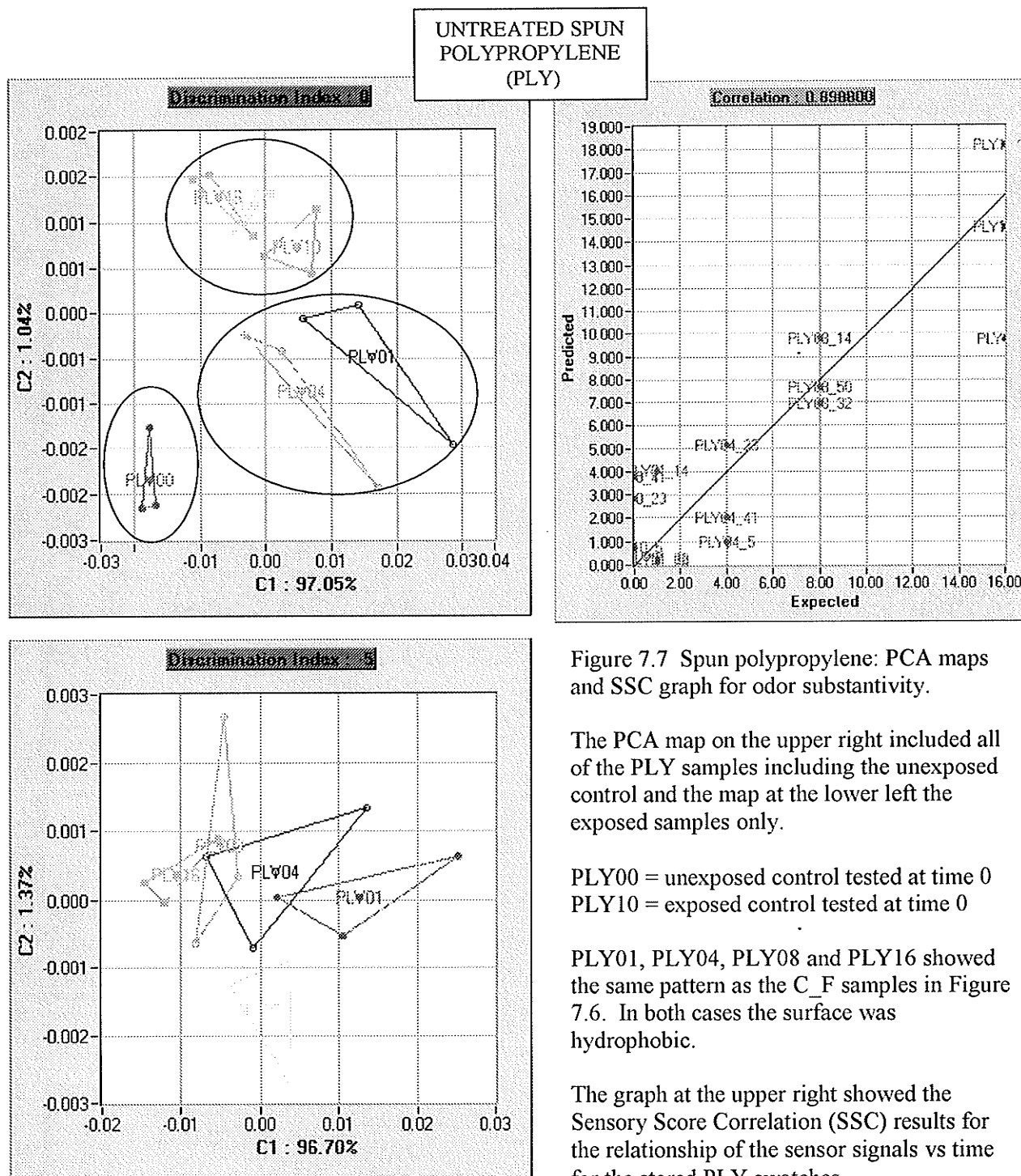


Figure 7.7 Spun polypropylene: PCA maps and SSC graph for odor substantivity.

The PCA map on the upper right included all of the PLY samples including the unexposed control and the map at the lower left the exposed samples only.

PLY00 = unexposed control tested at time 0
PLY10 = exposed control tested at time 0

PLY01, PLY04, PLY08 and PLY16 showed the same pattern as the C_F samples in Figure 7.6. In both cases the surface was hydrophobic.

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored PLY swatches.

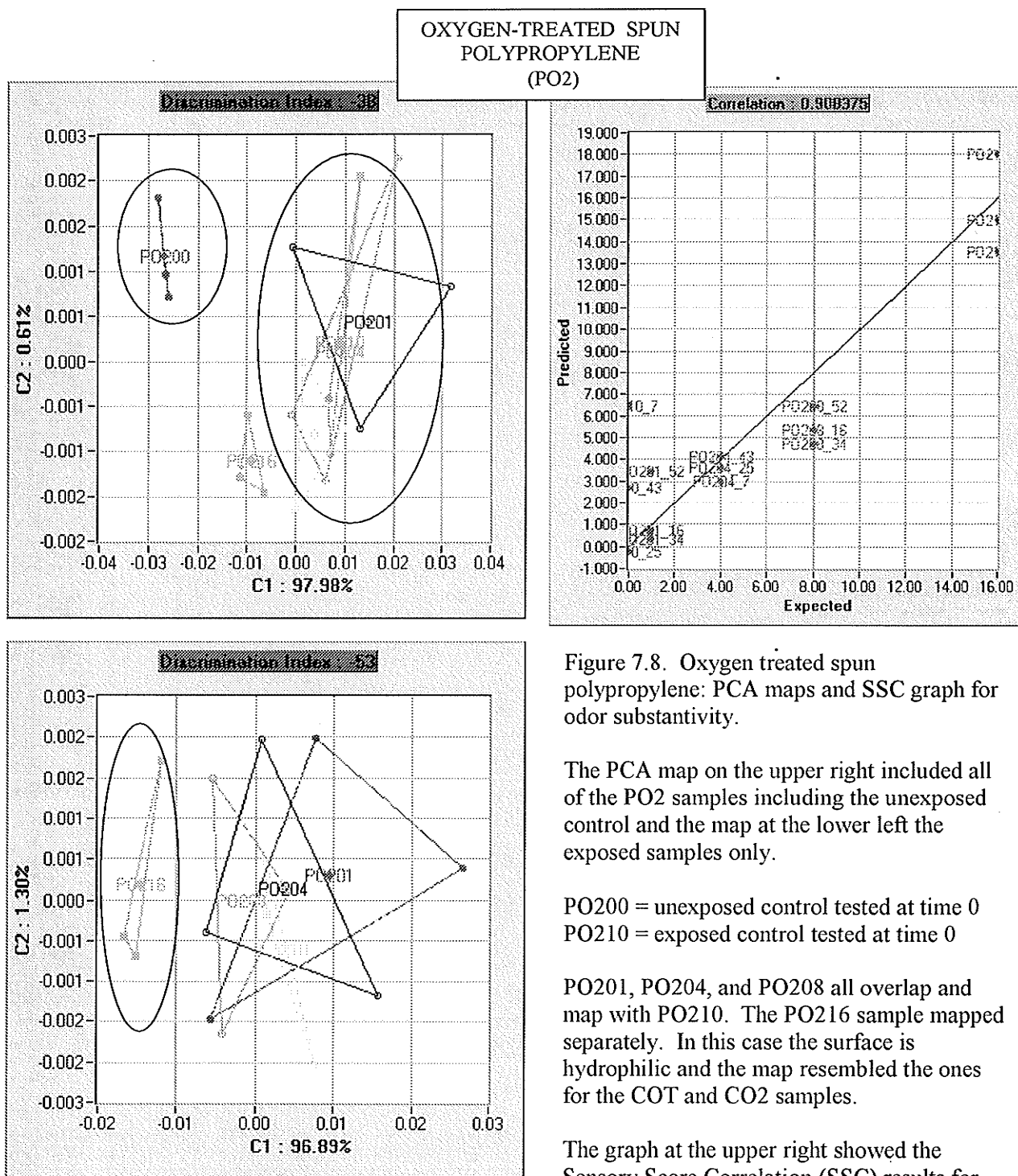


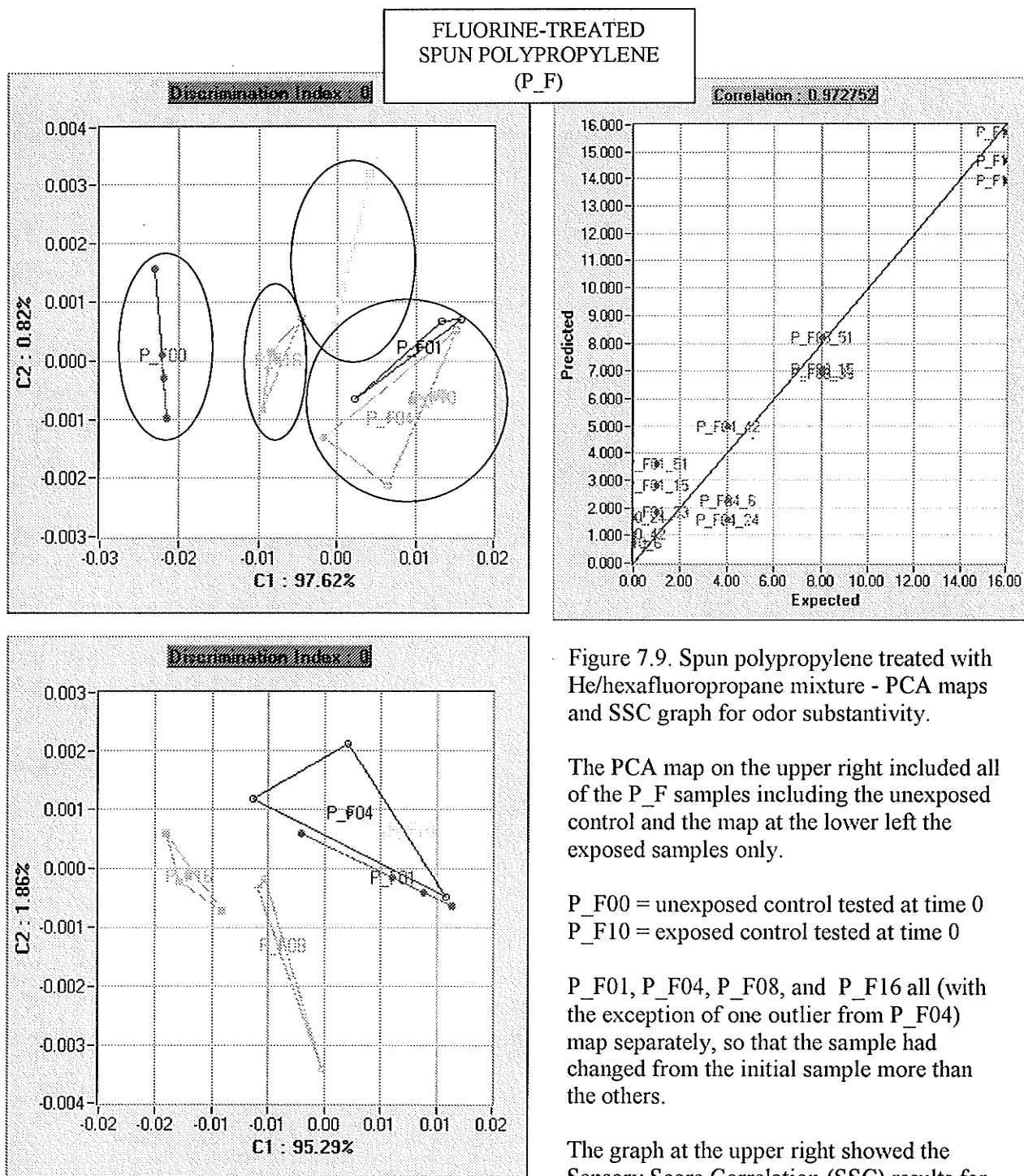
Figure 7.8. Oxygen treated spun polypropylene: PCA maps and SSC graph for odor substantivity.

The PCA map on the upper right included all of the PO2 samples including the unexposed control and the map at the lower left the exposed samples only.

PO200 = unexposed control tested at time 0
 PO210 = exposed control tested at time 0

PO201, PO204, and PO208 all overlap and map with PO210. The PO216 sample mapped separately. In this case the surface is hydrophilic and the map resembled the ones for the COT and CO2 samples.

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored PO2 swatches.



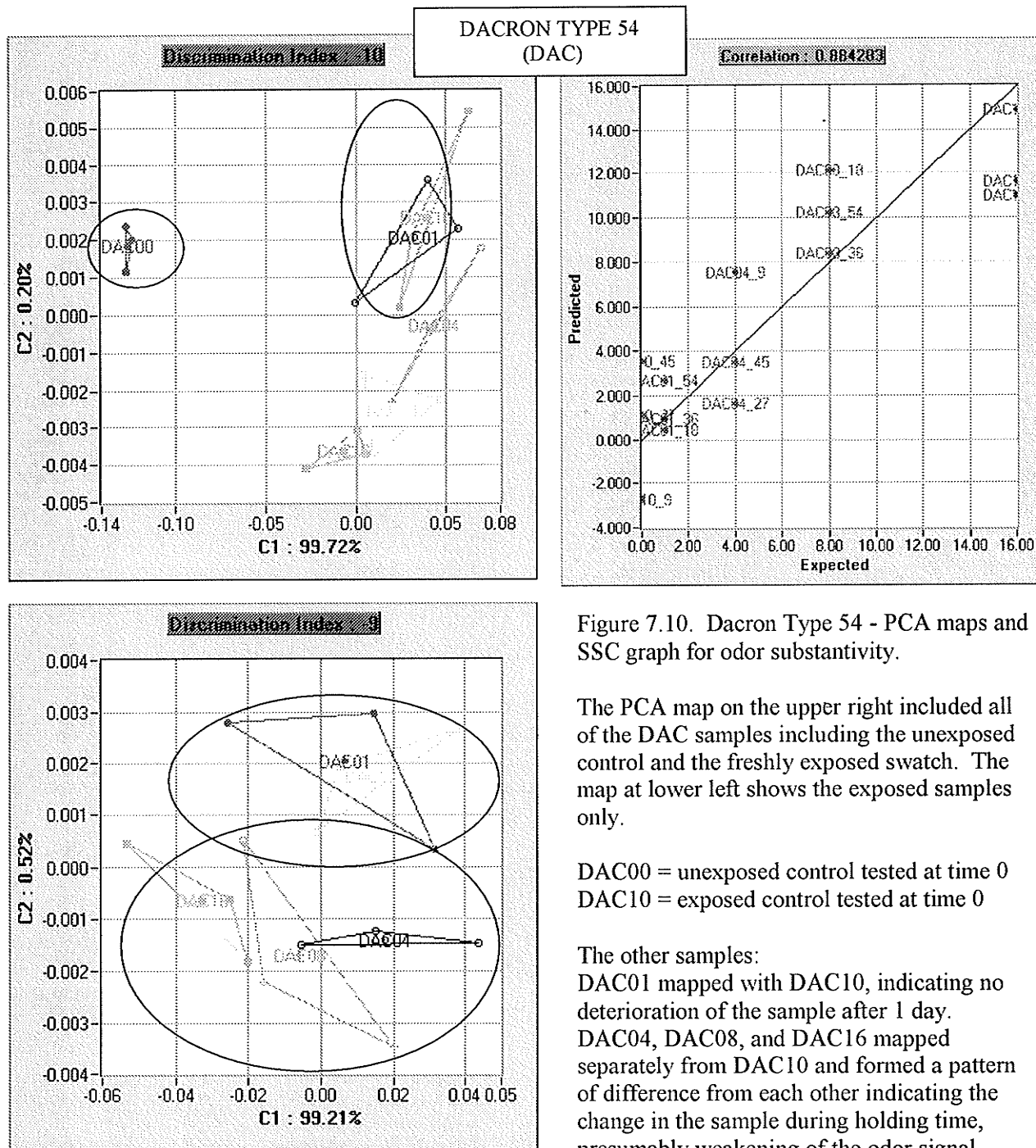


Figure 7.10. Dacron Type 54 - PCA maps and SSC graph for odor substantivity.

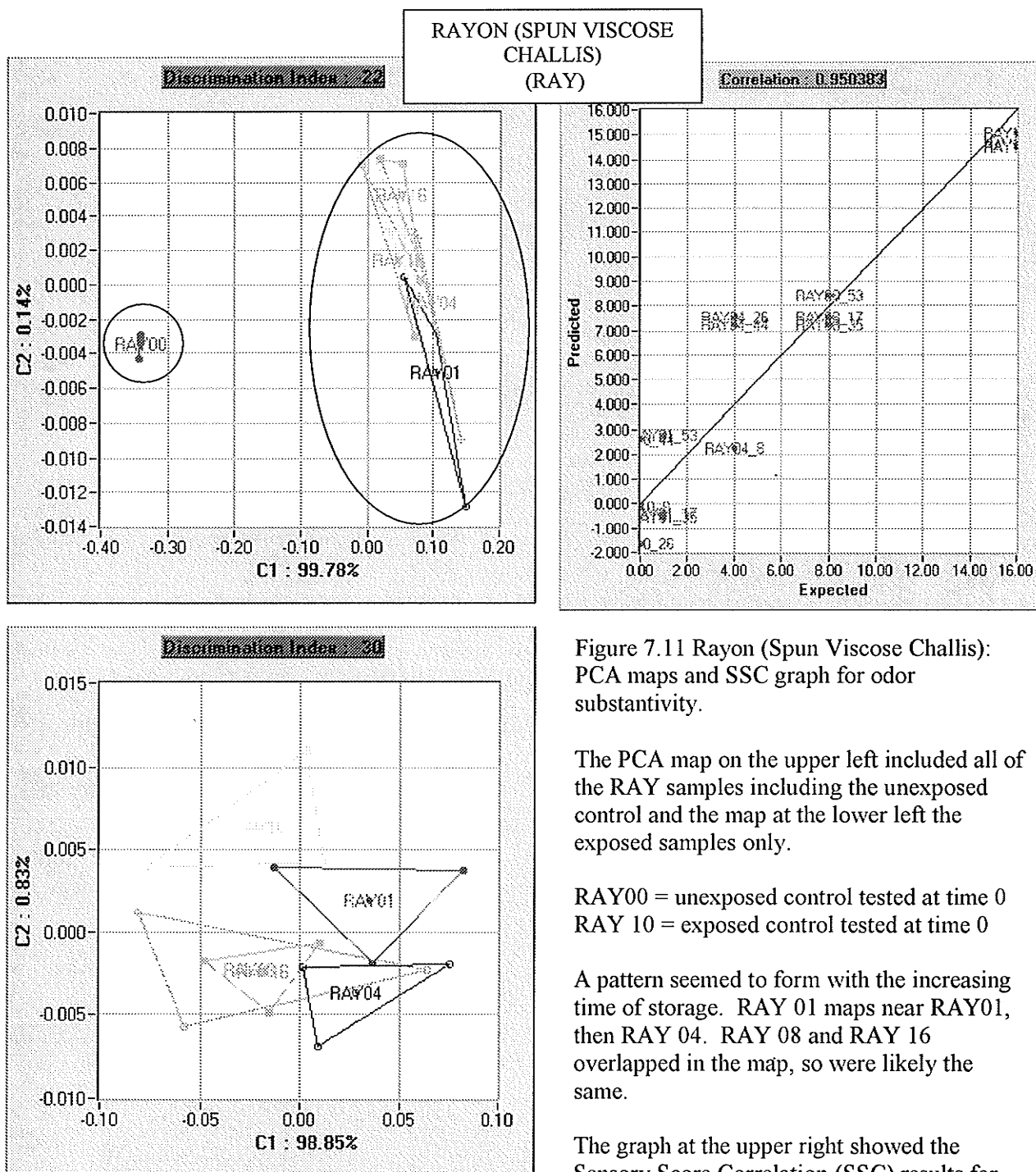
The PCA map on the upper right included all of the DAC samples including the unexposed control and the freshly exposed switch. The map at lower left shows the exposed samples only.

DAC00 = unexposed control tested at time 0
DAC10 = exposed control tested at time 0

The other samples:

DAC01 mapped with DAC10, indicating no deterioration of the sample after 1 day.
DAC04, DAC08, and DAC16 mapped separately from DAC10 and formed a pattern of difference from each other indicating the change in the sample during holding time, presumably weakening of the odor signal.

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored DAC switches.



ACTIVATED CARBON
CLOTH
- ACC -

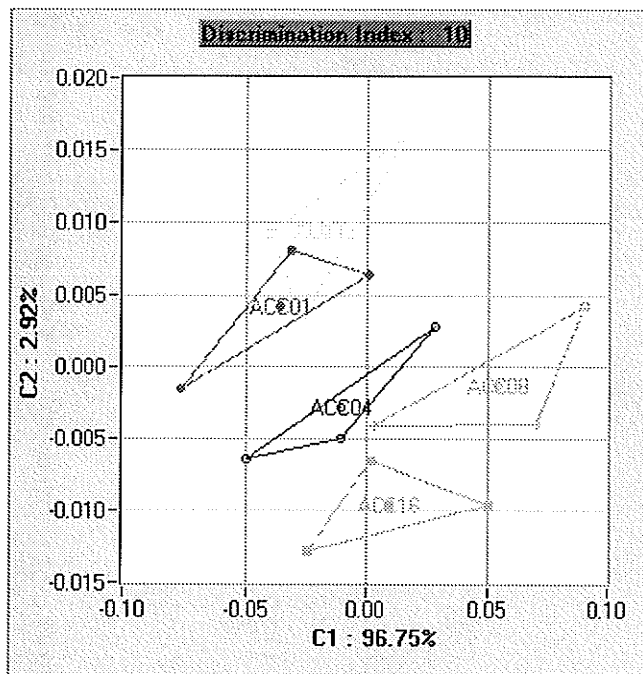
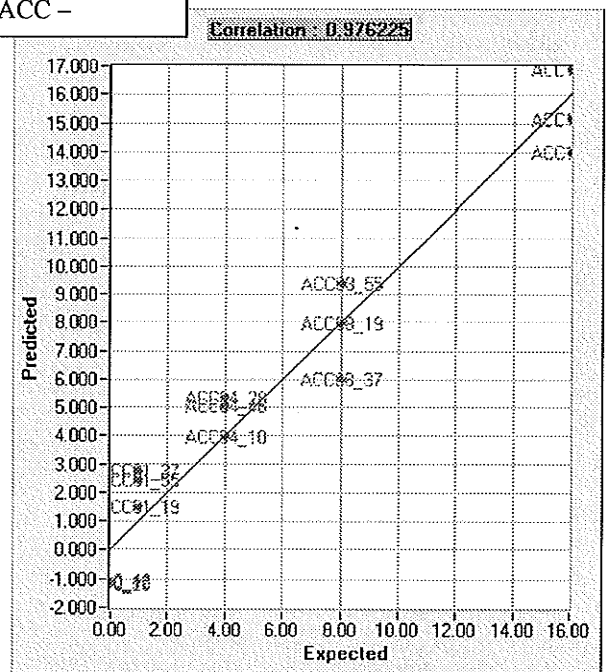
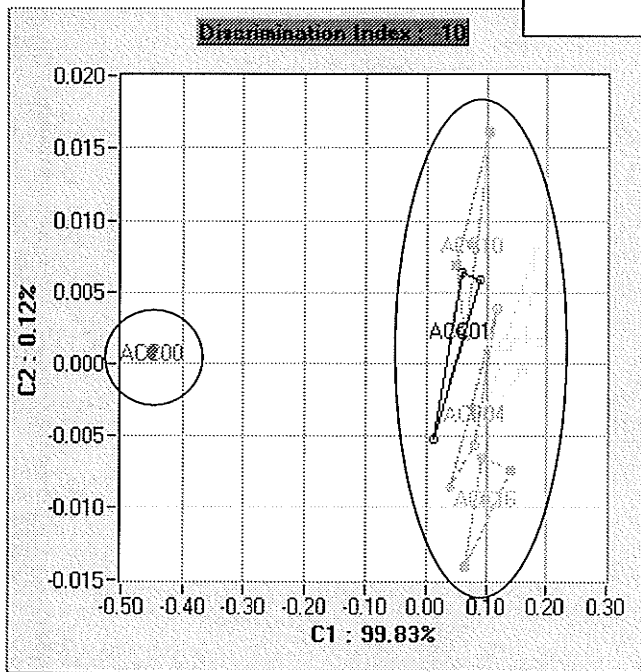


Figure 7.12 Activated Carbon Cloth: PCA maps and SSC graph for odor substantivity.

The PCA map on the upper left included all of the ACC samples including the unexposed control and the map at the lower left the exposed samples only.

ACC00 = unexposed control tested at time 0

ACC10 = exposed control tested at time 0

ACC01 mapped with ACC10. ACC04, ACC08 and ACC16 all mapped separately showing the change in the samples over time.

The graph at the upper right showed the Sensory Score Correlation (SSC) results for the relationship of the sensor signals vs time for the stored ACC swatches.

7.4 Conclusions

The treatments with O₂ and fluorine successfully changed the surface characteristics of each of the fabrics. The hydrophilic fabric became hydrophobic and the hydrophobic one hydrophilic, as shown by the change in the contact angle measurements and the ESCA results. When the samples were evaluated with electronic nose analysis, the helium/oxygen and the helium/C₃F₆ treatments did not appear to change the attributes of the cotton flannel for initial odor or for uptake of the swine odor simulant components onto the cloth. The spun polypropylene showed a different result, the untreated samples were all differently mapped according to the electronic nose; whereas the exposed control mapped differently to the exposed treated swatches. This change was reflected in the changes in the way in which the treatment was detected by the electronic nose. This change might be due to some etching of the fibres during plasma polymerization treatment, even though the treatment time was kept to 1 min to reduce this effect.

The substantivity test samples showed some interesting results. The correlation coefficients for the relationship of the sensor readings to the time in storage were ranged from 0.8843 to 0.9762, demonstrating that all of the samples showed a change in the nature of the sample that was correlated with the change in sensor reading. Presumably this change reflected a loss of the odorant from the surface of the cloth. This loss impacted back to the results from Study # 4 (see discussion there as well) in that the samples from two of the field tests had to be stored until analysis due to the breakdown of the autosampler system, which was part of the Fox 3000 system. This loss of adsorbed odorant meant that only the pre-test was analyzed within a time frame where little or no degradation of the samples might be expected and those were the samples that showed the best differentiation according to field conditions.

This swine odor simulant mixture was the one developed by Persaud et al. (1996). They noted that when this mixture was in the form of the basic solution (pH adjusted with ammonium hydroxide) it emphasized the ammonia component when the samples were tested with a conducting polymer array. When the pH was adjusted to be the acidic version, the fatty acid

components of the SOS were emphasized in the sensor responses. If this effect were operating here, one would expect a difference between the samples due to a difference in the components of the swine odor simulant which were being adsorbed. This effect did not occur. It is difficult to say at this point how the pH of the sample affected the stability of the samples, since all of them showed the change over time or to say how large the change was in terms of the intensities that might be assigned by a sensory panel.

Chapter 8

Summary of Results and Final Conclusions, New Findings and Recommendations for Research

8.1 Summary of Results by Study

The purpose of this research was to evaluate the potential role that cloth swatch testing and electronic nose analyses could play in environmental testing for agricultural malodors. Accomplishing this objective required several stages, the first of which was the acquisition of analytical systems (the electronic nose) and the development of methodologies for sampling and testing cloth swatches, and the second of which was the examination of the fabric performance for effectiveness and usefulness under laboratory and field conditions. This thesis described a series of five studies of varying complexity related to the stabilization of environmental malodors on cloth swatches and the sensory and electronic nose measurement with an Alpha MOS Fox 3000 system, of the presence and intensity of the odors adsorbed onto the fabrics.

In the Study #1, a 1-butanol reference scale commonly used in environmental testing for magnitude matching was evaluated using two sensory scaling methods, magnitude estimation and the labelled magnitude scale. The ratio data from each was used to calculate the constants of Stevens' Law. The calculated values of the exponent were $n = 0.59$ for magnitude estimation and $n = 0.46$ for the labelled magnitude scale. These were tested and found to be statistically different at $P < 0.001$, although well within the range of values for this exponent reported in the literature. The electronic nose could differentiate the samples to a high level of discrimination when the one sample that is below human threshold was eliminated. The electronic nose also correlated very well with both of the scaling methods. Since neither could be eliminated by performance, the decision as to which one to proceed with was made using the panelists' ease of response to the data collection and this was the labelled magnitude scale.

In the Study #2, 13 fabrics of varying fibres and structures were evaluated for their ability to adsorb malodors when exposed to a swine odor simulant under controlled conditions. Two methods of sensory scaling (difference-from control and labelled magnitude scale) and electronic

nose analysis with an Alpha MOS Fox 3000 were used to compare the samples both within and between sample sets. The purposes of this study were to identify and characterize standard fabrics that could be used to test malodor sampling, establish a laboratory exposure system and swine odor simulant to use for cloth swatch preparation, to acquire, install and establish protocols for an electronic nose system to evaluate malodors on cloth, and to use a sensory panel to evaluate malodors on cloth through a linear and a ratio scaling system. The data were used for three stage of analysis. The first analysis was comparisons within the fabric types selected to evaluate the individual fabric's ability to adsorb and retain swine odor. The main findings were as follows:

1. The exposure system and swine odor simulant were successfully used to create samples for sensory and electronic nose analysis in the Alpha MOS Fox 3000. Using these components, it was possible to establish the initial test conditions and protocols that allow stabilization of odors onto cloth swatches for measurement.
2. All of the fabric types tested were able to retain the swine odor simulant components to a level that could be perceived by the human sense of smell and could be measured through sensory testing. Cloth types could be generally identified from these results as more or less likely to be useful, so that the fabrics for further work could be chosen from the group of best performing fabrics.
3. The exposed cloth swatches were stable to analysis over the period of time of the sensory studies, i.e., for the same day preparation and four uses during testing.
4. Both scaling methods for collecting the sensory data were effective in evaluating the differences between the exposed and unexposed samples for odor uptake. Statistical analyses demonstrated these differences to be significant in all fabrics for both methods. Informal questioning for panelists' preferences for each of the scaling methods showed no clear preference for either method. All found both methods straightforward and easy to accomplish, so that the choice of method for future work is at the discretion of the

experimenter and the needs of the study.

5. Appropriate test conditions were established for electronic nose analysis of odors stabilized onto fabrics. The Alpha MOS Fox 3000 electronic nose data were successful in demonstrating the differences in exposed and unexposed samples for all fabric types used in the study. Therefore, it was a useful tool for the measurement of the presence of malodor in air samples. The electronic nose was also able to distinguish among the different unexposed fabrics used in the study. The sensitivity of the electronic nose system was in the appropriate range to compare the results of sensory responses and the e-nose responses.

In the second analysis, the differences among the fabrics for odor uptake following SOS-exposure were evaluated using analysis of variance and multiple comparison testing. The results showed the following relationships.

6. The groupings of fabrics for performance in odor adsorption from REGWF multiple comparisons were not very clear, as there is much overlapping of groups and mixing of the different fibre types. There were clear groupings for the lower mean scores for linen, cotton terry cloth, and activated carbon cloth and, of these, three fabrics would be eliminated from use in sensory testing. Activated carbon cloth, however, can still be of interest for use in testing with an electronic nose. It is designed to adsorb and retain odors, and would release the odors when heated, and so held potential for electronic nose analysis of environmental malodors.
7. The fabrics that both adsorbed and released odor to give the highest sensory means did not form a neat pattern based on fibre type or surface chemistry, but were distributed throughout both. The fabric that performed best for this was cotton knit (a cotton single knit), which was very difficult to manipulate due to its tendency to curl from its knit structure.

In the third part of this study, the measured physical attributes of the fabrics were compared to the sensory scores and to the sensor readings.

8. Multiple regression formulae were calculated for predicting sensory scores using the physical attributes of the fabric types. The r^2 values for the test within the cotton group was much higher than the relationship across all fabrics. These formulae are of limited use, in that they apply only within the fabrics tested in this study. However, they give an indication of which properties would be important in selecting other fabrics for testing. The formulae are shown as follows:

All fabrics included:

$$\text{LMS (log value)} = 1.7823 - 0.0012 (\text{FW}) - 0.4569 (\text{D}) + 0.0009 (\text{AP}) \text{ adjusted } R^2 = 0.4651.$$

$$\text{DFC} = 108.2146 - 0.0962 (\text{FW}) - 29.6684 (\text{D}) - 0.0429 (\text{AP}) \text{ (adjusted } R^2 = 0.6694).$$

The five cotton fabrics only:

$$\text{LMS (as log value)} = 1.2408 - 0.0019 (\text{FW}) + 0.0022 (\text{AP}) \text{ (adjusted } R^2 = 0.9924).$$

$$\text{DFC} = 66.06803 - 0.1263 (\text{FW}) + 0.0575 (\text{AP}) \text{ (adjusted } R^2 = 0.8375).$$

Where, FW = fabric weight in g/m^2

D = density in g/cm^3

AP = air permeability in cc/cm^2

LMS = predicted value for odor intensity on labelled magnitude scale (as a log value)

DFC = predicted value for odor intensity on difference from control scale

From this, higher sensory scores for the same treatment were associated with lower fabric weight and density and higher air permeability when all fabrics were included. When only cotton fabrics were used, density was a constant, and higher sensory scores for the same treatment were associated with lower fabric weight and higher air permeability.

9. The electronic nose data were examined for relationships between the sensor readings for the exposed swatches and the physical attributes measured for the fabrics. The sensor readings were most highly correlated for the synthetic and the protein fibers with fabric weight, air permeability, porosity and thickness. Correlation coefficients were not as high for cotton samples and for cotton plus linen samples for fabric weight and thickness, and were poorer

for all other relationships. Fabric density, which was a constant for each fiber, was somewhat correlated with the sensor signals for the exposed fabrics.

All fabrics adsorbed odor to some degree and both sensory panels and the electronic nose were able to detect the changes reliably. The groupings of fabrics for most and least effectiveness could be identified, however fabrics which functioned in the mid-range were not distinguishable. When the physical attributes of the fabrics were related to the sensory scores, those with lower fabric weight and density and higher air permeability were identified as being most useful and when tested within cottons, the important factors were lower fabric weight and higher air permeability. Substantivity of odors was shown for the short term in the second study in the evaluation of the re-use of samples by sensory panelists up to four times. While activated carbon cloth did not perform well in sensory analysis, the adsorbed swine odors were released during electronic nose analysis. The nature of this fabric, which is designed to adsorb and retain odors, placed it in the group of fabrics that would be explored in further testing.

In the third study, the available GC/MS was unsuccessful in providing the headspace composition of the sensory and electronic nose samples of the SOS-exposed fabrics. This meant that the question of “which components are adsorbed and released from the cloth during laboratory exposure of the cloth swatches” could not be answered with this data. Suggested methods for accomplishing this are discussed, however financial assistance was not available at this time to further explore this at this date.

Data manipulation using the software associated with the electronic nose allowed the removal of the cloth signal from the swine odor simulant-exposed cloth signal. Using the programming with the electronic nose, the sample headspace could be evaluated separately from the cloth swatches. From the patterns of mapping in the principal component analysis maps, the similarities of headspace could be demonstrated. While this result should be confirmed by further testing, the evidence is that the spun polypropylene sample gave a headspace sample which most closely resembled the components of the solution. The signals from ammonia, skatole, and acetic

acid appeared to be different from the grouping of the other components and consistently mapped separately and closer to the residual signals from the various cloth swatches.

In the fourth study, selected cloth swatches were exposed to malodors in a field situation simultaneously with the collection of sensory data during an odor dispersion study. This work, a system for collecting cloth swatch data simultaneously with sensory data was demonstrated under field testing conditions in an odor dispersion study. The resulting swatches could be transported to the laboratory for analysis in an appropriate time frame of up to a 1-day holding time for analysis in an electronic nose system.

The results from September 14 indicated that both the activated carbon cloth and the spun polypropylene samples able to retain an odor sample in the field and were differentiated by distance by the PCA program. The comparisons of the sensory data with the sensor responses for each of these cloth swatches showed a greater correlation between the sensory values and activated carbon cloth than with spun polypropylene. This would indicate that activated carbon cloth would be the fabric substrate of choice in a field-testing situation for electronic nose analysis. The spun polypropylene had performed well in Study #2 in the laboratory sensory tests where the air speed of odor exposure was much lower and could also continue to be used in a laboratory test situation. Limited useful comparisons could be made for the remaining fabrics due to the breakdown of the autosampler at the beginning of the analysis of the September 21 samples. Given that, it was still possible to make some comparisons, allowing for the deterioration of the samples. In general, activated carbon cloth showed the highest correlation coefficients when related to the sensory data, even under adverse testing conditions, reinforcing that it is likely the fabric which would be of most use for field sampling.

When electronic nose analysis was compared to the sensory results for actual field conditions, activated carbon cloth was found to be the most appropriate of the cloth sources tested, although spun polypropylene performs well when the windspeed is very low.

In the final study, the effect of surface chemistry on the adsorption of odors was evaluated through changing a hydrophilic fabric (cotton flannel) and a hydrophobic fabric (spun polypropylene) through He/O₂ and He/ C₃F₆ exposure in a plasma polymerization unit. Surface changes in the fabrics were validated through contact angle measurements and ESCA analysis.

When the samples were evaluated with EN analysis, the helium/oxygen and the helium/C₃F₆ treatments did not appear to change the attributes of the cotton flannel for initial odor or for uptake of the SOS components onto the cloth nor did they change the initial odor of the sample. The spun polypropylene showed a different result – the untreated samples were all differently mapped according to the EN, while the exposed control mapped differently to the exposed treated swatches. This change was reflected in the changes in the way in which the treatment was detected by the EN. This change might be due to some etching of the fibres during plasma polymerization treatment, even though the treatment time was kept to 1 minute to reduce this effect.

The substantivity test samples showed some interesting results. The correlation coefficients for the relationship of the sensor readings to the time in storage were ranged from 0.8843 to 0.9762, demonstrating that all of the samples showed a change in the nature of the sample which was correlated with the change in sensor reading. Presumably this reflected a loss of the odorant from the surface of the cloth. This impacted back to the results from Study #4 in that the samples from two of the field tests had to be stored until analysis due to the breakdown of the autosampler system which was part of the Fox 3000 system. The data from these two days was at best inconclusive – unlike the clearer patterns from the first sampling day when the samples were analyzed immediately.

This SOS mixture was the one developed by Persaud et al. (1996). They noted that when this mixture was in the form of the basic solution (pH adjusted with ammonium hydroxide) it emphasized the NH₃ when the samples were tested with a conducting polymer array. When the pH was adjusted to be the acidic version of the artificial swine odor, the fatty acid components of

the SOS were emphasized in the sensor responses. If this effect were operating here, one would expect a difference between the samples due to a difference in the components of the swine odor simulant which were being adsorbed. This did not occur. It is difficult to say at this point how the pH of the sample affected the stability of the samples, since all of them showed the change over time or to say how large the change was in terms of the intensities which might be assigned by a sensory panel.

8.2 Conclusions Related to Overall Research Questions

A series of research questions was given in the Introduction and these questions formed the basis of the studies included here.

The first question was: *How do different scaling systems perform for sensory measurement of malodors? Humans perceive most sensory stimuli on a log scale and most studies relating sensory perception of intensity to physical measurements rely on this fact. A new measurement method has been developed by Green & co-workers (1993, 1996) based on the work of Georg that allows the collection of sensory intensity data that is ratio scaled but using a pen and paper system. It has performed well in other systems, and we will evaluate it here compared to standard magnitude estimation methods.*

Two of the studies compared different sensory methodologies for measuring odor intensity in odor systems associated with malodors. When two methods of ratio scaling, magnitude estimation and the labelled magnitude scale, were compared for testing odor intensity in a series of 1-butanol concentrations, they each produced a calculated exponent of Stevens' Law which was consistent with other published values. When linear scaling (the difference from control test) and ratio scaling (the labelled magnitude scale) were used to evaluate the intensity of malodors in cloth swatches treated with a swine odor simulant, both scaling systems were able to differentiate among the cloth types. The labelled magnitude scale performed well in both of these applications, however, the other methods did also. From this result, the selection of the scaling

test could be based on the needs of the study. If calculations requiring ratio data were needed, then the labelled magnitude scale could be used. If comparisons were required between treatments in a study, either the labelled magnitude scale or the difference from control test could be used.

The second question was: *How do different types of cloth perform for the uptake of odors? Is there a fibre that is better for this and are there any physical properties of the cloth that will help predict this performance?* Different cloth types performed differently in the exposure studies and cloth types could be identified that performed well and that did not. There was no pattern of higher levels of odor uptake intensity being associated with a particular fibre or cloth structure. Cellulose fibres comprised both the best and the worst performers, with cotton knit being one of the best and cotton terry cloth being one of the worst. Linen, which has a very crystalline structure, did not adsorb odor well. All of the fabrics adsorbed odor to some degree, and differentiation of the groups based on performance was difficult. When physical properties of the fabrics were evaluated compared to their odor uptake performance, the factors of density, fabric weight and air permeability were most important physical attributes. When this was considered only within cotton fabrics, fabric weight and air permeability were most important. Higher scores would be associated with lower fabric weight and density and with higher air permeability.

Cotton flannel was the fabric that has been most often used in swatch studies reported to date. From the results in these studies, it performed well for odor adsorption, as did several other fabrics. In electronic nose studies of the adsorbed odor components, spun polypropylene seemed to adsorb a pattern of odor that was most similar to the swine odor simulant. In the field studies, the activated carbon cloth seemed the most stable for adsorbing and retaining odors when higher wind-speed was present.

The third question was: *Are there differences in the odorants that different fibres or cloth types will adsorb? Which components are most easily adsorbed and released into the system and*

how can this be assessed? This question was only answered in a limited way, due to problems with the GC/MS analysis of the samples. The data from manipulation of the electronic nose patterns, showed that spun polypropylene seemed to adsorb a pattern of odor that was most similar to the swine odor simulant used as the odor source. A complete answer to this question will require another study using appropriate GC/MS testing.

The fourth question was: *How well does this laboratory methodology carry forward into actual field-testing? Can cloth types identified under laboratory conditions be successfully utilized an actual odor dispersion test format?* A method of collecting cloth swatch samples simultaneously with sensory data was devised and applied during an actual odor dispersion study. Problems with the autosampler system for the electronic nose made the timely analysis of two of the sample sets impossible, so that only results from a single limited set of swatches were really useful. From this set, activated carbon cloth appeared to be the most useful cloth source for field sampling under real weather conditions. The factor of breakthrough was likely the most significant effect here, with activated carbon cloth being the most resistant to this.

The fifth question was: *Can cloth surfaces be made to adsorb odors more efficiently for this work?* Plasma polymerization was used to change the surface of two of the fabrics, cotton flannel and spun polypropylene. The treatments added either –OH groups to the surface (made the fabric more hydrophilic) or fluorine to the surface (made the fabric more hydrophobic). The electronic nose results for the cotton showed that all three of the cotton samples mapped together, so that presumably the treatments did not improve the odor adsorption over that of the untreated control. The results for the spun polypropylene showed that both the treated swatches mapped to suggest that they had adsorbed a greater intensity of the odorant compared to the untreated control.

The sixth question was: *Which measurement systems will allow odors to be evaluated? New technology in the form of sensor-based electronic nose technology is available. How well does this compare to the use of human assessors for the presence and intensity of malodors*

sampled from the environment? In this work, all of the measurement systems were successful in allowing malodors to be evaluated. Sensory testing using different scaling methods worked well in assessing malodors stabilized onto different types of cloth. The electronic nose also performed well and held promise as a means of analyzing the odors at levels that are equivalent to those perceived by the panelists.

In summary, this work has resulted in several steps in methodology development for the study of cloth swatches for environmental sampling which include:

- Further development of the laboratory protocols for exposures of cloth swatches for evaluation of base materials – including cloth preparation and treatment, identification of a swine odor simulant and identification of sources and types of standardized fabrics for use in this testing method.
- The development of protocols for the use of electronic nose analyses for evaluation of the adsorption of environmental malodors onto cloth. (This also included the acquisition of an electronic nose system, followed by an extended period of training and experience – both in the operation and in the repair of the autosampler component of the system.)
- The development of a viable method of field testing cloth swatch odor adsorption. To this end, a field vest was designed and the protocols for actual on-location testing were developed.
- The application of new methods of textile processing, i.e., surface modification through the application of plasma polymerization to fabrics to enhance their odor adsorption performance.

The general performance of the fabrics is summarized in Table 8.1. From this it can be seen that both spun polypropylene and activated carbon cloth showed the most promise as suitable cloth substrates for laboratory and field sampling respectively.

8.3 Recommendations for Further Work

There were several avenues of research that could be pursued based on the work in these studies. The first was continuation of the GC/MS work to establish the odorants that were present in the headspace of the samples from the different cloth sources. This work would clarify the components of swine odor that were available to the sensory panel and to the electronic nose for odor evaluation. This GC/MS analysis could also be used to evaluate the headspace sample for other applications of the cloth swatch testing and aid in establishing fabrics for specific applications in conjunction with electronic nose analyses, since one fabric may not be the answer to all testing situations. Other test situations that have been suggested include the presence of extraneous chemical compounds as applied to specific aspects of crop testing, and security screening for disallowed products in passenger and cargo situations. Further work on field collection of environmental malodors would include the use of activated carbon cloth and the stabilization of odors for longer periods of time to allow the shipment of samples for electronic nose testing. The development of the electronic nose applications of cloth swatch testing would also include the use of artificial neural networks as the decision-making component of the test system.

Table 8.1 Summary of observations on the performance of fabric types for adsorption of environmental malodors			
#	Sample Code (electronic nose)	Fabric Description	Comments
1	COT	cotton - flannel, bleached	The cotton samples did not behave as a group – the performance for odor uptake was variable from “best” to “worst”. This was not completely explainable – considering that all of the fabrics were constructed from cotton, which was not given any treatments during the weaving or knitting processes. Structurally, cotton fibres are a “collapsed tube” – with odors reported as being relatively evenly distributed across the whole fibre cross-section (Liu et al., 2004) and provided a large surface area for odor adsorption.
2	CTB	cotton broadcloth, bleached, mercerized, combed	
3	CTK	cotton - knit - bleached cotton t-shirt fabric	
4	CTT	cotton - 9.5 oz, bleached terry cloth	
5	CTW	cotton - twill, bleached, mercerized	Cotton flannel had been the fabric of choice in most cloth swatch work for sampling environmental odors, however it did not appear to do the best job. The choice to use it was likely based on its occurrence as a clothing fabric for workers – the odor was perceived on this fabric – swatches of it were used in sampling. It performed moderately well in uptake of odorant in laboratory conditions (low airflow rates), but did not seem to work well in actual field conditions. The cotton single knit used here adsorbed odor well, however was extremely difficult to handle as a sampling medium because of its tendency to “roll”, a result of its construction. Cotton twill and cotton broadcloth performed about as well as the cotton flannel, but the cotton terry cloth performed poorly, having a lower perceived odor from the same level of exposure. Whether this was a result of the larger volume of fibre in a given swatch actually inhibiting the release of the odor was not known. However, the cotton terry cloth had almost 3 times the weight of fibre in the swatch as cotton flannel and more than 2.5 times that of the cotton single knit.
9	LIN	linen - suiting	Linen performed poorly in this test – however this was not surprising when its structure is compared to that of cotton. While it was another cellulose fibre, it had very long polymer units and a very crystalline structure. Its fibres were smooth and had less surface area than the cottons (as shown by the lower porosity values).

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Chapter 9

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Appendix A

Informed consent information for sensory panel participants.

Sensory Panel Recruitment Information

Project Title: Measuring uptake of malodors onto cloth swatches for development of a new field test method.

The purpose of this study is to evaluate a new method of collecting airborne malodors for laboratory measurements. The odors are collected on cloth swatches and in this study we are comparing different fabrics for the ease of adsorption of odors. The odors are from a model system based on the malodors perceived in and near hog barns.

Note: The study is being run under the standards set forward by the Ethics Review Committee, Faculty of Human Ecology, University of Manitoba and will involve informed consent for each stage of the tests.

There are three stages in the project:

1. A selection panel using weak 1-butanol solutions to validate ability to perceive low levels of off-odors.
2. Training sessions to familiarize each participant with the procedures involved – a calibration procedure
3. Actual evaluation sessions using the test samples.

The tasks: sniffing samples and recording intensity of perceived odor on a paper ballot.

The time involved: - all panel sessions will be either in late morning or mid-afternoon

- at least 2 selection panels (10-15 minutes each),
- 2 familiarization sessions (15 min each)
- 24 data collection sessions (up to 15 min each)

As a thanks for your participation: On completion of all of the data collection sessions, you will receive an honorarium of \$150.00 as a U of M Bookstore gift certificate.

Investigator: Roberta York
CFIA Sensory Science/University of Manitoba
Telephone: 983-5086

CONSENT FORM

Project Sensory Assessment of Agricultural Malodors
Title: _____

Principal Investigator(s) Martin W. King Tel: 474-9913
Name(s): Roberta K. York 983-5086

Address: Sensory Science Laboratory, Canadian Food Inspection Agency
501 University Crescent, Winnipeg, MB, R3T 2N6

Names of 1. Dr. Q. Zhang 2.
Co- Dept. of Biosystems Engineering
Investigator(s): U of Manitoba

Please tick either YES or NO in response to each of the following questions:

1. Do you understand that you have been asked to be in a research study? Yes ☐ No ☐
2. Have you read the information sheet or heard the verbal explanation of the investigator? Yes ☐ No ☐
3. Do you understand the benefits and risks involved in taking part in the research study? Yes ☐ No ☐
4. Have you had an opportunity to ask questions and discuss the study? Yes ☐ No ☐
5. Do you understand that you are free to withdraw from the study at any time without having to give a reason and without any detriment to your ongoing association with the University of Manitoba, the Department of Fisheries and Oceans, or the Canadian Food Inspection Agency? Yes ☐ No ☐
6. Do you understand that you can refuse to answer any questions or provide information during your participation in the study? Yes ☐ No ☐
7. Has the issue of confidentiality been described to you and do you understand: a) who will have access to the information you provide, b) that no reports will identify you as an individual? Yes ☐ No ☐

I agree to take part in this study Yes ☐ No ☐

Signature of Participant

Printed Name of Participant

Date

Two copies of this form are provided for you to complete, one of which you are expected to keep. The second copy will be kept by the principal investigator.

Thank you.

INFORMATION LETTER

Project Title: Sensory Assessment of Agricultural Malodors

Principal Investigator(s) Name(s): Martin W. King
Roberta K. York

Tel: 474-9913
983-5086

Address: Sensory Science Laboratory, Canadian Food Inspection Agency
501 University Crescent, Winnipeg, MB, R3T 2N6

Names of Co-Investigator(s): 1. Dr. Q. Zhang
Dept. of Biosystems Engineering
U of Manitoba

2.

The following information is given in order to provide you with the basis for informed consent for your participation in the sensory studies of agricultural malodors.

1. The purpose of this research is to develop a new standard method for the analytical sensory evaluation of malodors from agricultural sources. The results will be used to guide the further study of these malodors and the methods by which these odors can be reduced or eliminated from large-scale livestock rearing production facilities.

The project involves 1) the standardization of the sensory methodologies for quantitative measurement of malodor intensity - for laboratory, animal research, and on-site environmental testing, and, 2) the development and testing of improved methods of sampling of air-borne odors through the development of odor-sensitive fabrics. This will provide a new standard test and protocols to evaluate odors and allow meaningful cross-comparisons of the results from different test situations. It will also provide the basis for a provisional standard for regulatory testing.

2. The odors used in the study, while unpleasant, are not harmful.

a) There will be no health risk to subjects who are participating in the study - the odorants which are part of the standard odor system, although strong-smelling are all naturally-occurring breakdown products of protein, fat and carbohydrates. The components of the odor system are all known compounds and have been used for many years in other aspects of odor research. These compounds are perceptible in the parts per million and parts per billion ranges of concentration. As the testing involves only odorants, panelists will not be exposed to the ingestion of any of the odor mixture components.

b) The benefits to the participants include: the knowledge of contributing to research in an area which has potential economic benefits to the Province of Manitoba, the opportunity to test sensory skills in a controlled environment, and, an expression of our appreciation in the form of either a gift certificate for the U of M Bookstore or cash.

3. All of the panel work in this project is in the category of analytical sensory testing which uses selected and trained panelists who have demonstrated necessary basic sensory skills for odor perception and the

ability to perform the intensity-scaling tasks required. Tests will involve the smelling of odors from specific sampling sources and evaluating their presence and/or intensity using various measurement scales. There are three stages in participation in the study:

- Candidate Selection for participation: using standard ASTM (American Society for Testing and Materials) and ISO (International Standards Organization) methods - usually two or three sessions per person.
- Training Sessions: using various odor standards for evaluation and training - up to eight sessions per panelist.
- Data Collection Procedures: using prepared samples of known composition and air samples obtained from on-site testing at livestock-holding facilities. The number of experiments and the number of sessions per experiment will vary, but will be discussed at the beginning of each panel series.

For example: To evaluate the effect of storage time of exposed swatch samples, 10 panelists would be selected and trained in intensity assessment of the odors. Samples would be drawn and prepared for 5 to 8 storage times (days) and presented to the panelists as a sample set. The sets would be tested over at least three replications of the series. In any given sample session, panelists would be required to evaluate from 5 to 25 samples, depending on the test design, with the provision (requirement) for the use of time and appropriate rinsing materials (usually sniffing a sample of distilled water). The sessions are conducted in a sensory science laboratory, i.e. comfortable, quiet surroundings, equipped with a positive pressure, activated-carbon filtered air system, florescent day-lights at 5000°K (noon daylight).

4. This research is completely separate from any services, benefits or rights whatsoever that each participant may have access to now or in the future from the University of Manitoba, the Department of Fisheries and Oceans, or the Canadian Food Inspection Agency (whichever is appropriate).

5. You are free to withdraw from the study at any time without having to give a reason and without any detriment to your ongoing association with the University of Manitoba, the Department of Fisheries and Oceans, or the Canadian Food Inspection Agency (whichever is appropriate).

6. All information collected during the study will be kept confidential and no individual will be identified in the analysis of the results. Each participant is assigned a code number and all data taken from the sensory ballots will be coded with this number. Data will be held at the by R.K. York at the Sensory Science Laboratory of the Canadian Food Inspection Agency, located at the Freshwater Institute. Access to the raw data will be limited to the principal investigator, the co-investigators and to the Sensory Laboratory Technician.

Dr. Martin W. King, Advisor
Department of Clothing and Textiles
University of Manitoba
474-9913

Roberta K. York, M.Sc., Ph.D. Student
Canadian Food Inspection Agency
501 University Crescent, Winnipeg, MB, R3T 2N6
983-5086

Appendix B

Ballot for selection tests in study #1 – triangle tests using 1-butanol.

Agricultural Malodor Evaluation Studies

Odor Sensitivity Testing

Name _____

Date _____

Series _____

You have been given six sets of 3 samples each. Within each set, 2 samples are the same and 1 is different. Please test each of the samples in a set and select the odd sample by its odor using the following method:

Raise the cover of the flask and, using 2 or 3 shallow sniffs, evaluate the odor present in the sample and replace the cover immediately. Test the samples in the order presented. You may evaluate each sample more than once if needed – leave the cover on the sample for a minute to allow the sample to equilibrate.

Open the flask only briefly to reduce any odor level in the test room.

If no difference is apparent, you must guess.

Sample Set	Odd Sample

Comments:

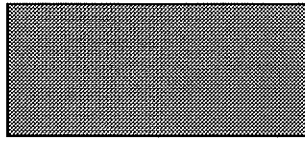
Appendix C

Ballots used for training in the use of the magnitude estimation for measuring sensory intensity.

NAME _____

DATE _____

MEASURING PERCEPTION WITH RATIO SCALING



This is the Reference Sample "R"
- give it a value of "10"

Rate the size of each of the boxes below relative to the "R" sample.

If it seems twice as large, call it "20",

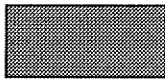
If it seems 1/4 as large, call it "2.5"

If it seems the same, call it "10"

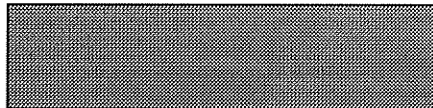
There is no limit to the size of the
numbers or fractions you can use.

Size of Sample Relative to "R"

1.



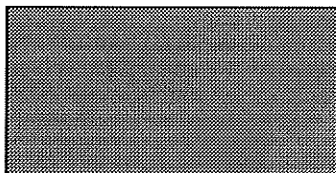
2.



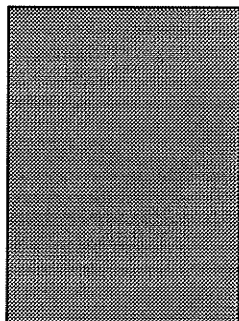
3.



4.



5.



Appendix D

Ballot used for the collection of the magnitude estimation data for the 1-butanol scale.

Name: _____

Date: _____

Samples: _____

Test Series: _____

MEASURING ODOUR INTENSITY

You have been given a reference sample, coded "R" and a series of number-coded samples which contain different intensities of the test odour, 1-butanol.

Evaluation Method: Lift the lid from the flask enough to be able to sniff the contents. Take one shallow sniff, then 1 or 2 more, as needed. Replace the lid on the flask. Rinse between samples by sniffing the flask of distilled water provided. You must rinse between samples.

Evaluate the sample coded "R" and assign the intensity of the odour you perceive a value of 10. Evaluate each of the coded samples, and rate the intensity of the odour relative to the reference sample. e.g. If it seems twice as strong, give it a value of 20, 10 times as strong, give it a value of 100. If it seems one-quarter as strong, give it a value of 2.5.

There is no limit to the multiples or fractions you can use to describe the intensity of the odour.

SAMPLE CODE	PERCEIVED INTENSITY

COMMENTS:

Appendix E

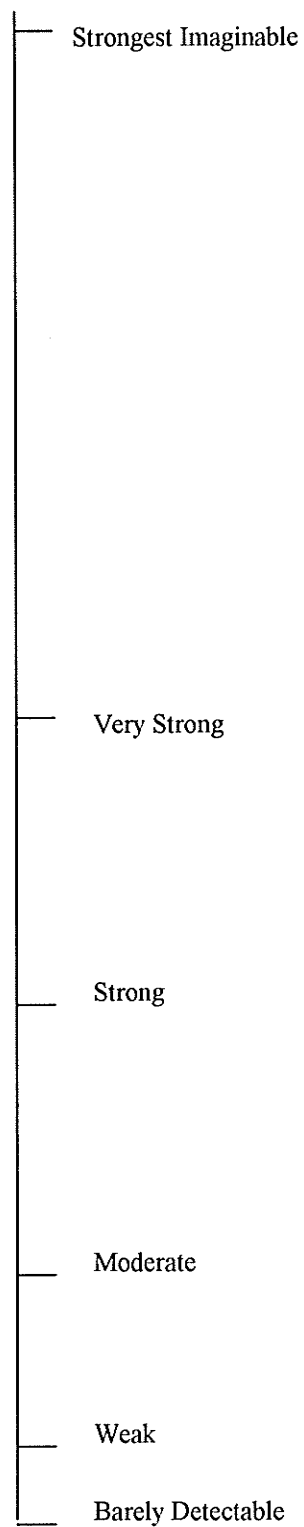
Ballot used for the collection of the labelled magnitude scale data for the 1-butanol scale.

Scaling Odor Intensity

Name _____

Date _____

Code _____



Comments:

Appendix F

Ballot used for the collection of the difference-from-control data of odor intensity for swine odorant-exposed cloth swatches.

Agricultural Malodor Studies

DIFFERENCE FROM CONTROL TEST

SCALING ODOR INTENSITY

Name: _____

Date: _____

Series: _____

Instructions:

1. Smell the sample marked "R" first, then smell the "warm-up" sample.
2. Rate the amount of difference between these samples as "extremely different from R". Please mark the scale accordingly.
3. Continue with the coded samples. Mark the scale to indicate the amount of the overall difference from "R"
4. Please rinse by sniffing the distilled water between coded samples.

Code No.

(actually a 6-inch (150 mm) line scale – truncated for publication)

_____	same as R	extremely different from R
_____	same as R	extremely different from R
_____	same as R	extremely different from R
_____	same as R	extremely different from R
_____	same as R	extremely different from R
_____	same as R	extremely different from R
_____	same as R	extremely different from R

COMMENTS:

Appendix G

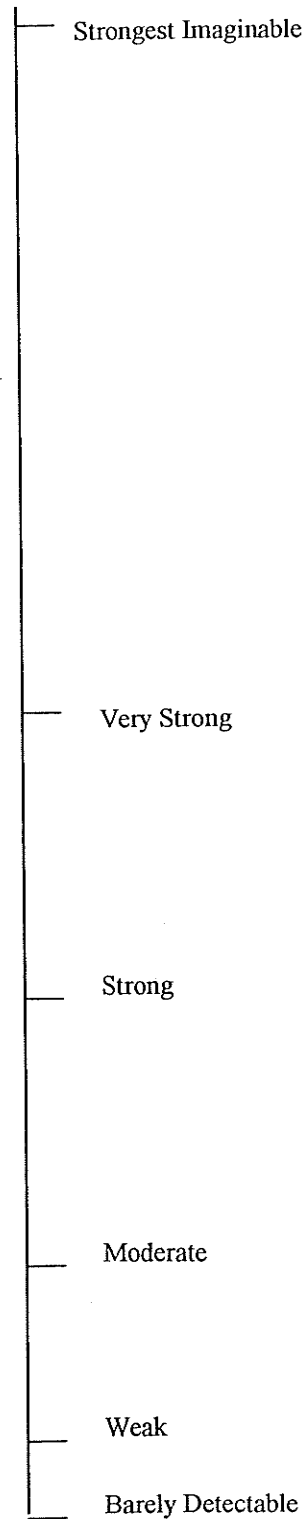
Ballot and instructions used for the collection of the labelled magnitude scaling data for odor intensity of swine odorant-exposed cloth swatches.

Scaling Odor Intensity

Name _____

Date _____

Code _____



Comments:

Instructions to Panelists for Odor Evaluations

Scaling Odor Intensity

Smell the sample labelled 'warm-up' and rate it as you would one of the coded samples. Do this only once at the beginning of the test

Rinse with distilled water (by sniffing) and wait 1 minute (timed) before beginning the samples.

Rate the intensity of each of the coded samples on the scale provided.
The end points are defined as

none = no odor present

strongest imaginable = the strongest odor you can imagine perceiving

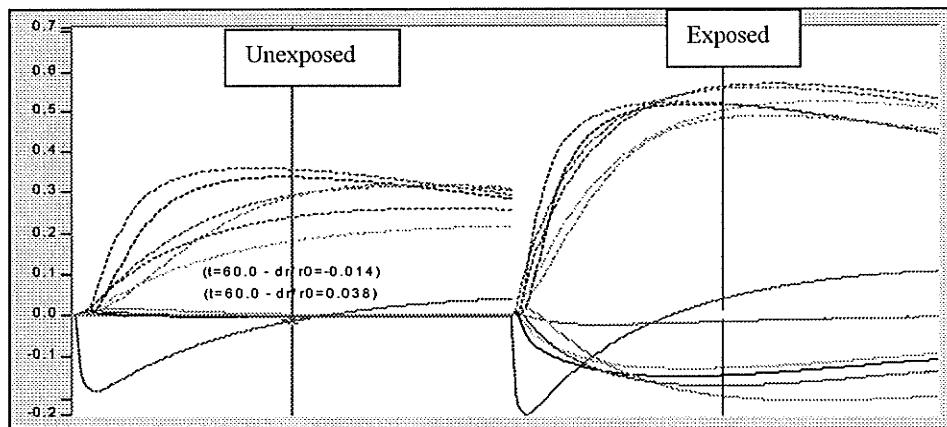
Rinse by smelling distilled water between samples and wait 1 minute (timed) between samples.

Many thanks for your participation!

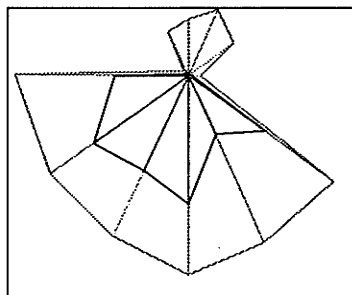
Appendix H

- . Response curves for each of the 12 sensors for the 2-minute data acquisition period
for each of the 13 fabrics tested at three incubation temperatures

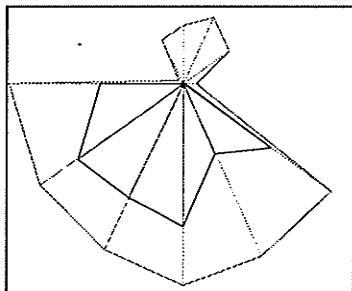
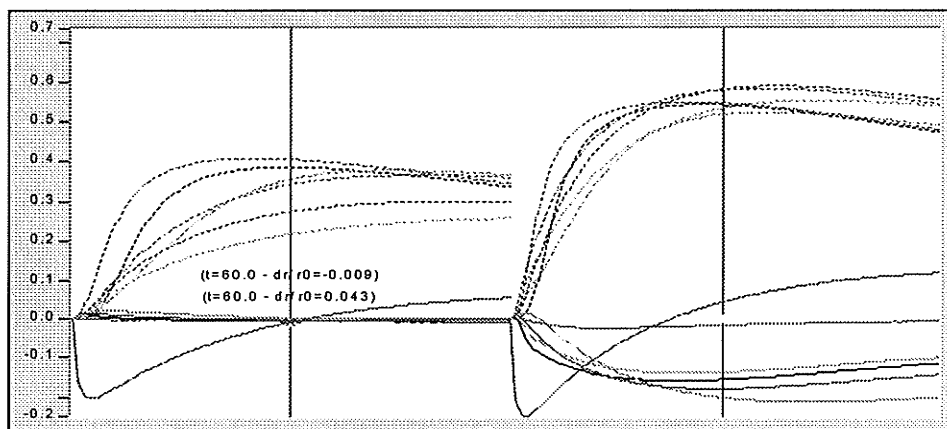
1a. Cotton Flannel - Unexposed and Exposed (Exposed) Swatches - incubated at 35°C



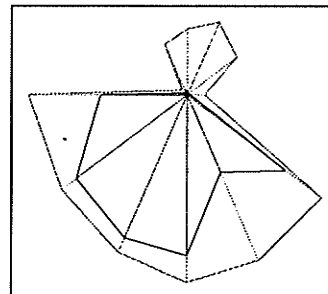
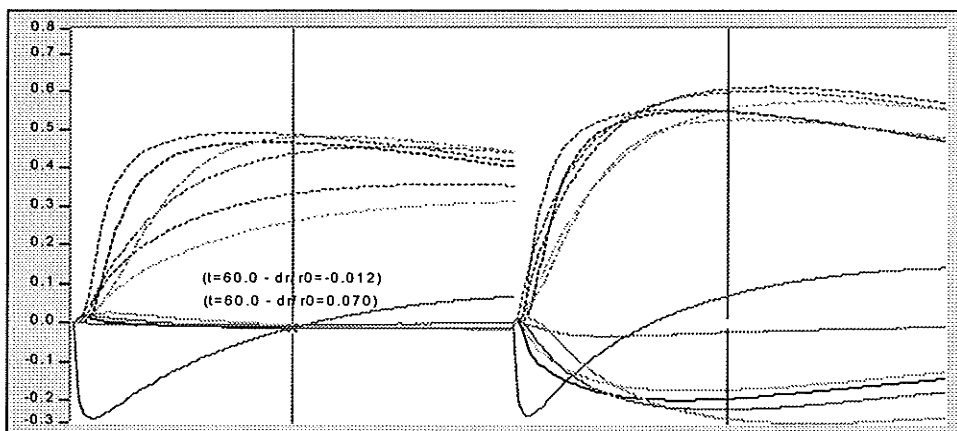
“Star” diagram of maximum response of each of the 12 sensor –
Black line = unexposed
Red line = exposed with swine odor simulant



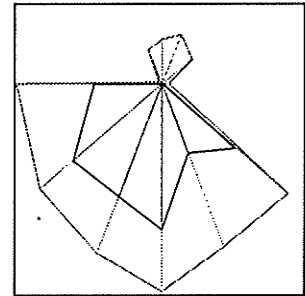
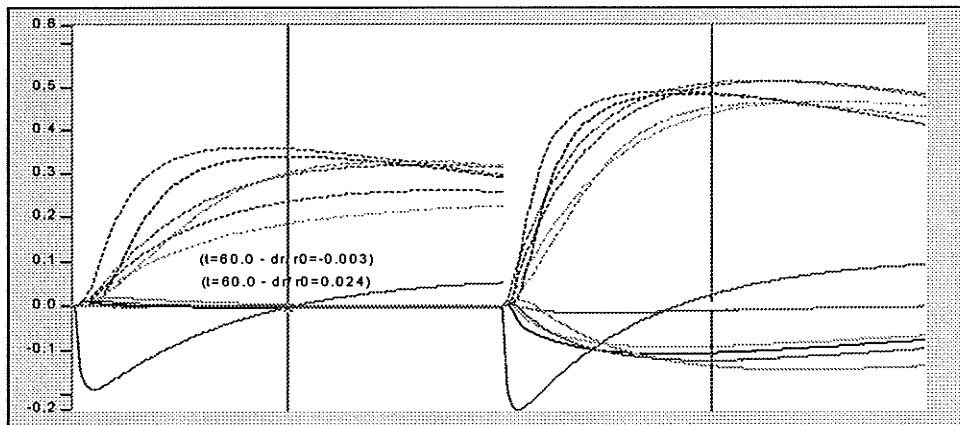
1b. Cotton Flannel - Unexposed and Exposed - incubated at 40°C



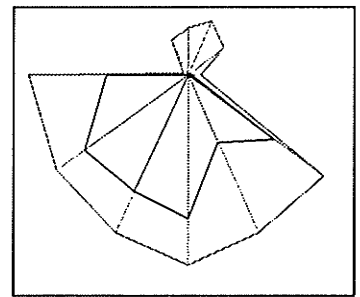
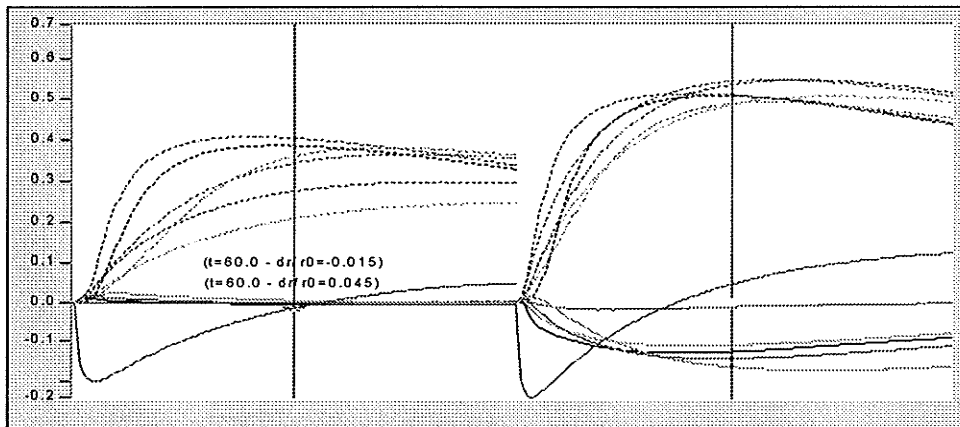
1c. Cotton Flannel - Unexposed and Exposed – incubated at 60°C



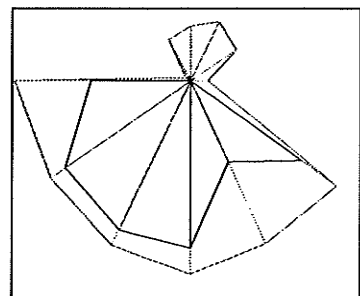
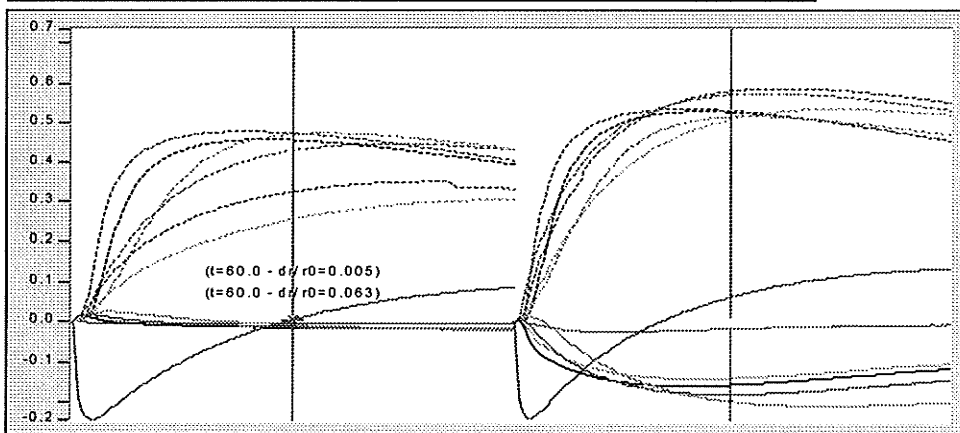
2a. Cotton Broadcloth – Exposed and Unexposed – incubated at 35°C



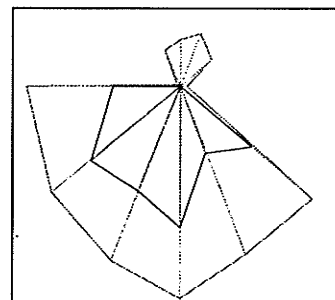
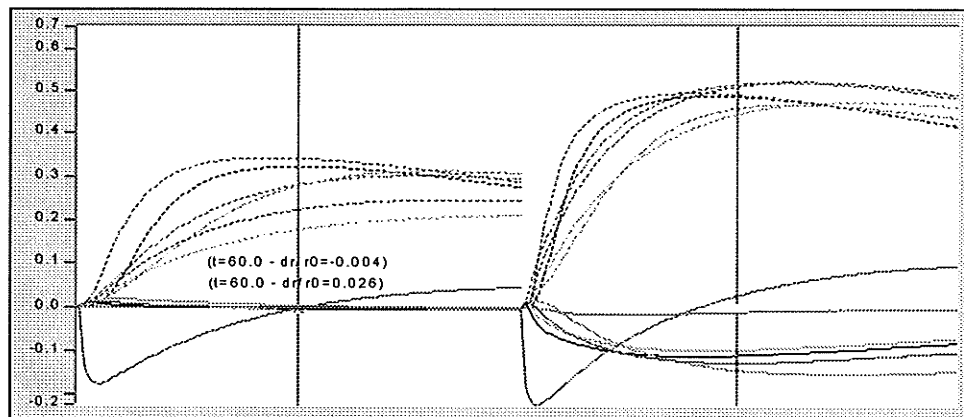
2b. Cotton Broadcloth – Exposed and Unexposed – incubated at 40°C



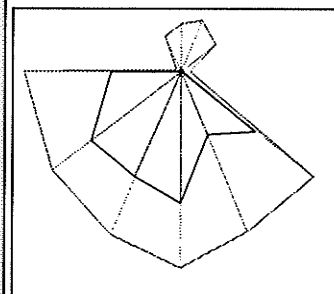
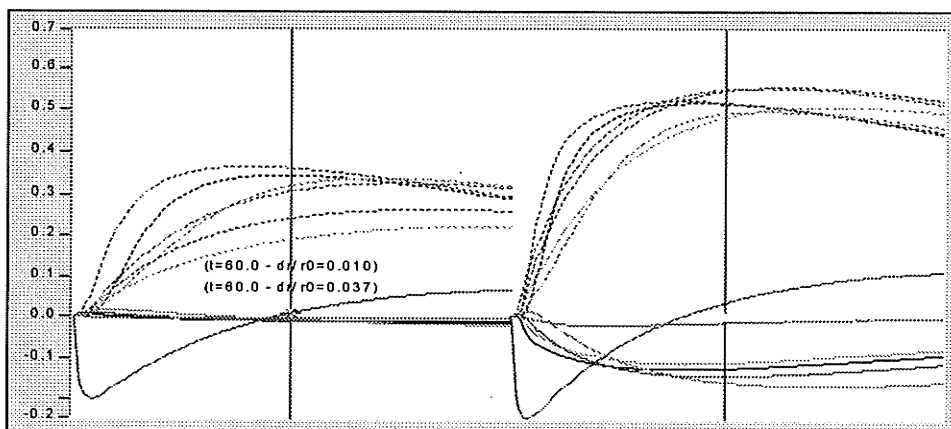
2c. Cotton Broadcloth – Exposed and Unexposed – incubated at 60°C



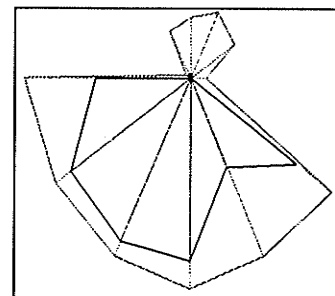
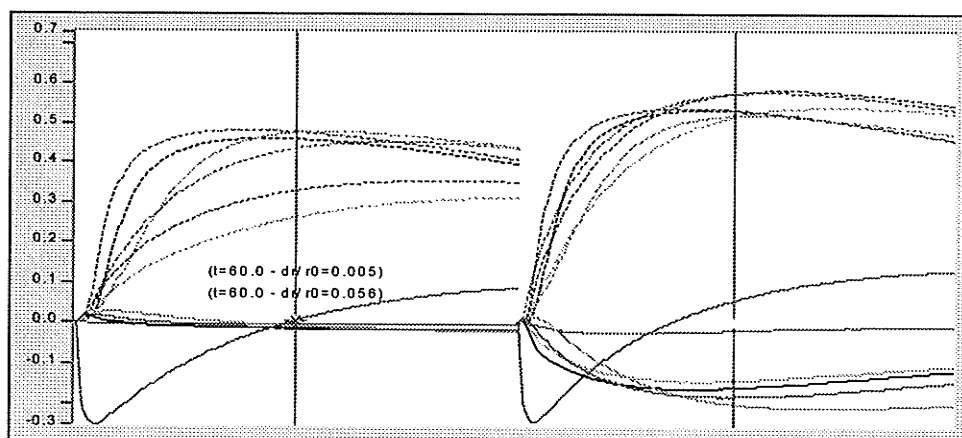
3a. Cotton Knit – Exposed and Unexposed – incubated at 35°C



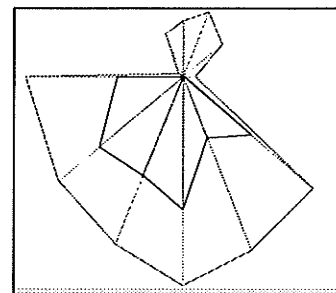
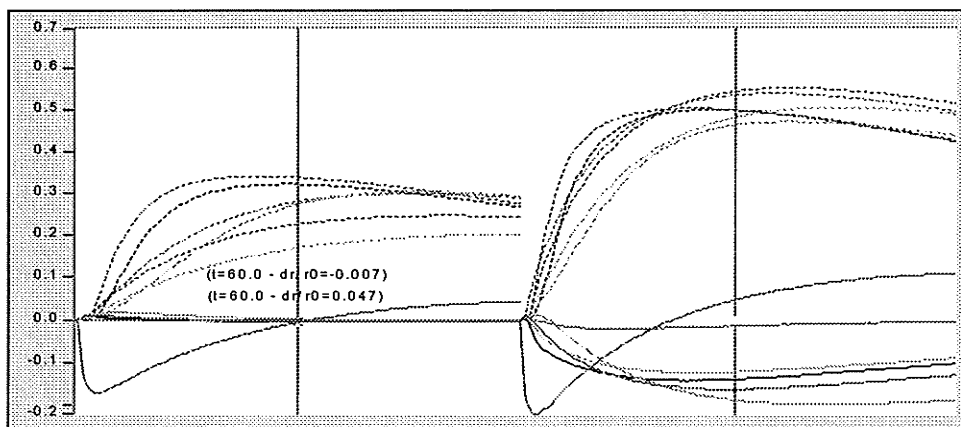
3b. Cotton Knit – Exposed and Unexposed – incubated at 40°C



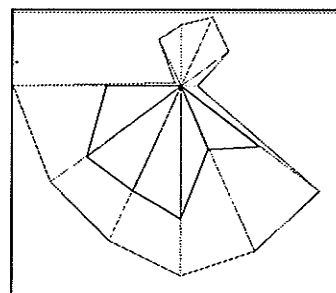
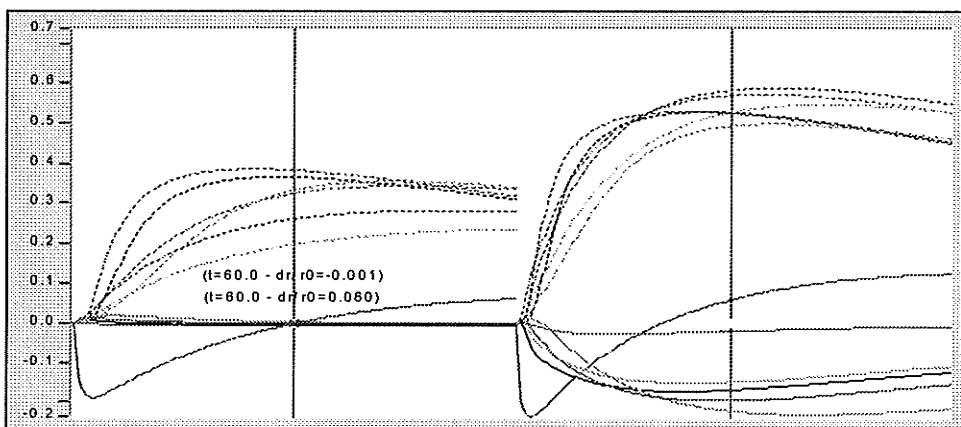
3c. Cotton Knit – Exposed and Unexposed – incubated at 60°C



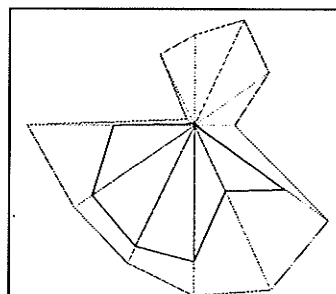
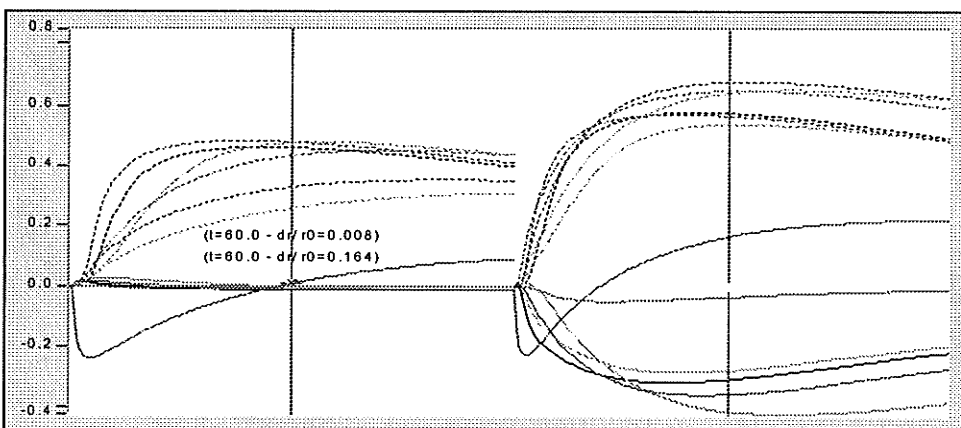
4a. Cotton Terry Cloth – Exposed and Unexposed – incubated at 35°C



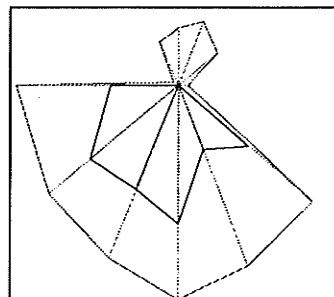
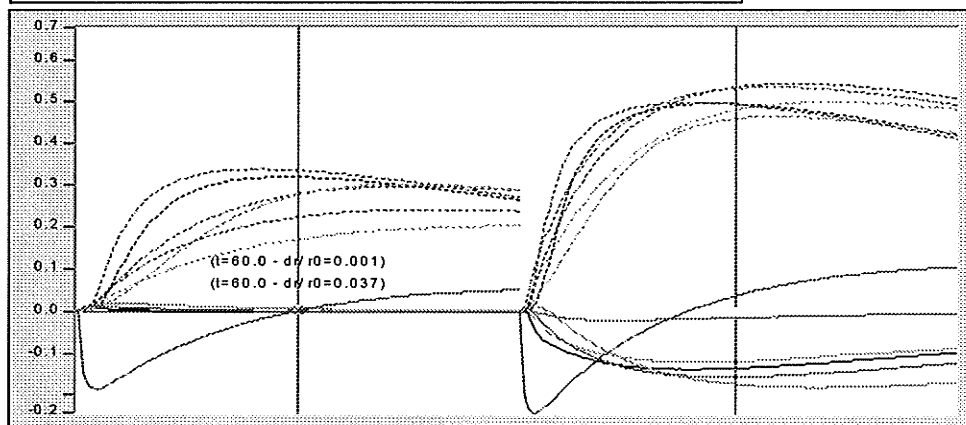
4b. Cotton Terry Cloth – Exposed and Unexposed – incubated at 40°C



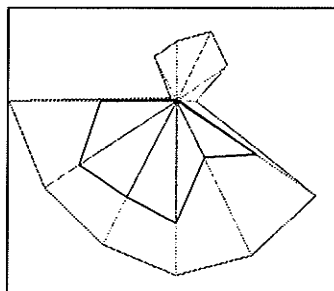
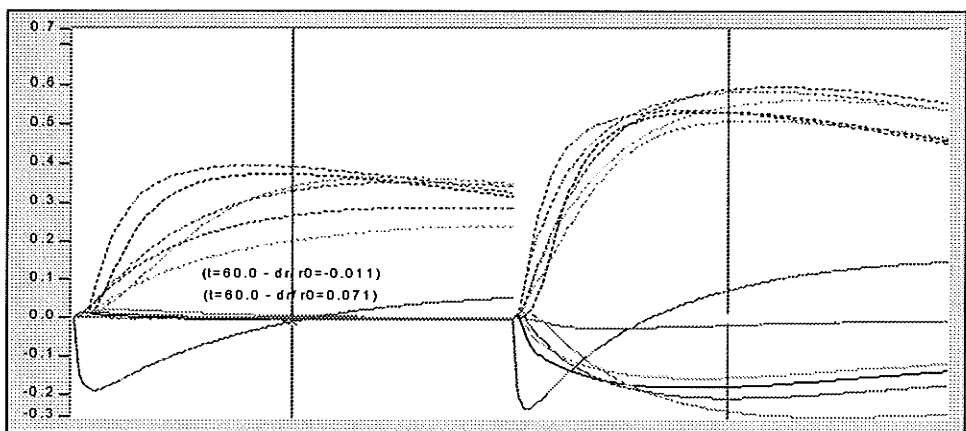
4c. Cotton Terry Cloth – Exposed and Unexposed – incubated at 60°C



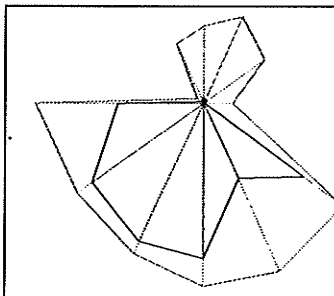
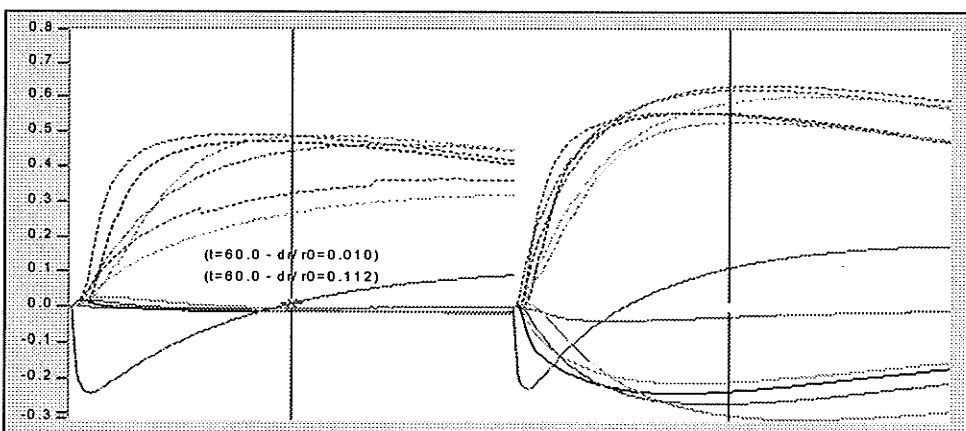
5a. Cotton twill – Exposed and Unexposed – incubated at 35°C



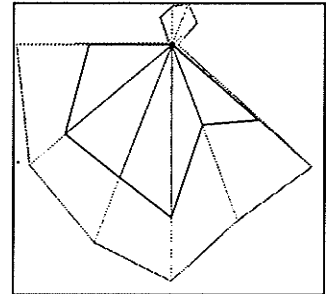
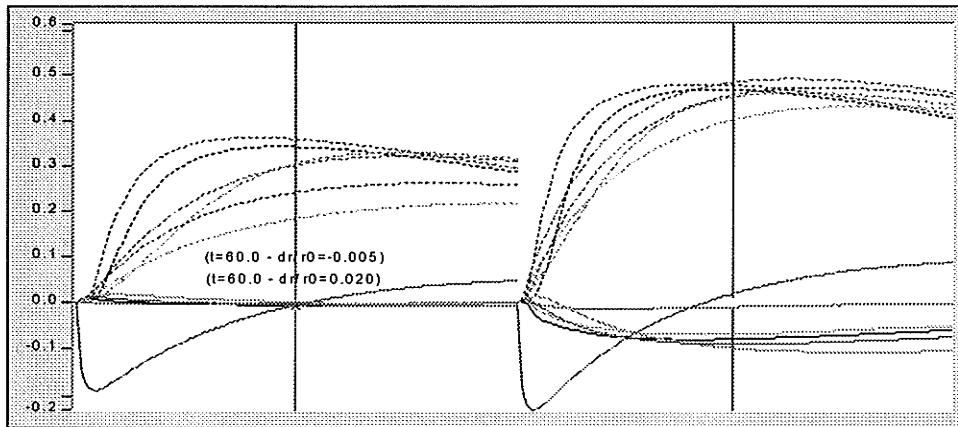
5b. Cotton twill – Exposed and Unexposed – incubated at 40°C



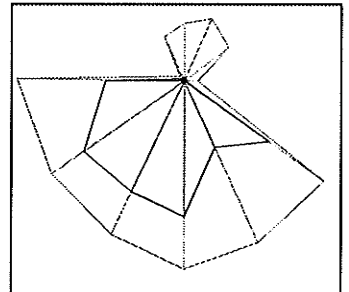
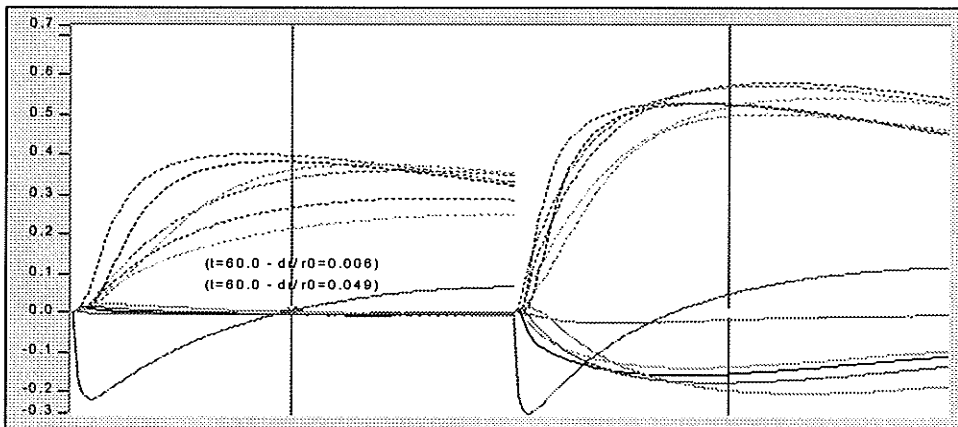
5c. Cotton twill – Exposed and Unexposed – incubated at 60°C



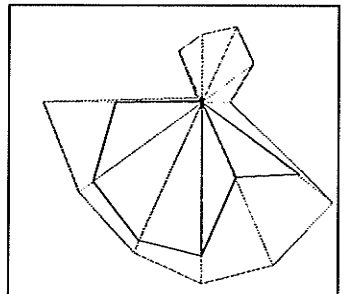
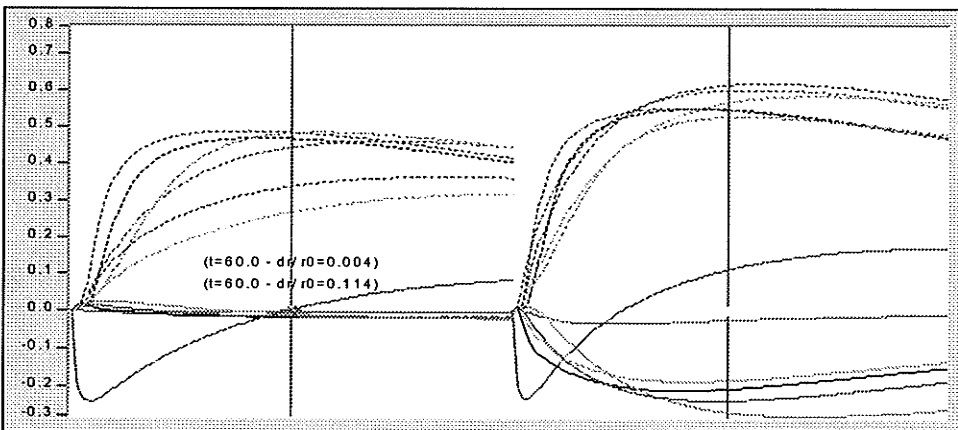
6a. Wool Flannel – unexposed and exposed – incubated at 35°C



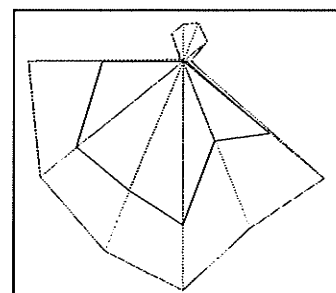
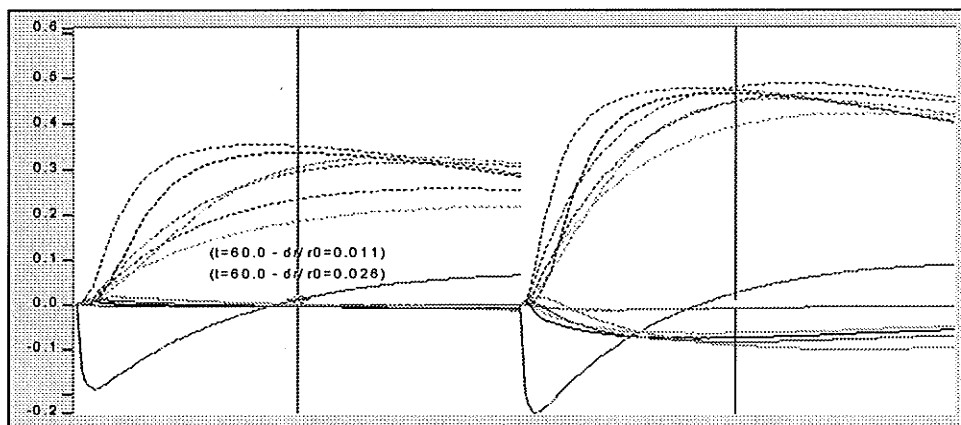
6b. Wool Flannel – unexposed and exposed – incubated at 40°C



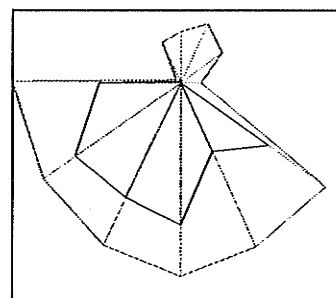
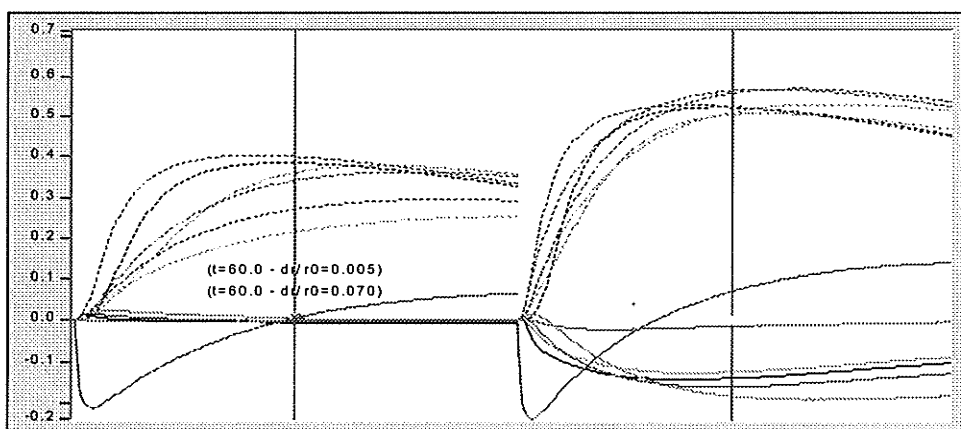
6c. Wool Flannel – unexposed and exposed – incubated at 60°C



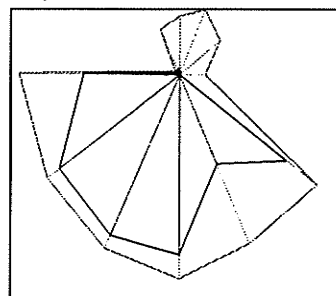
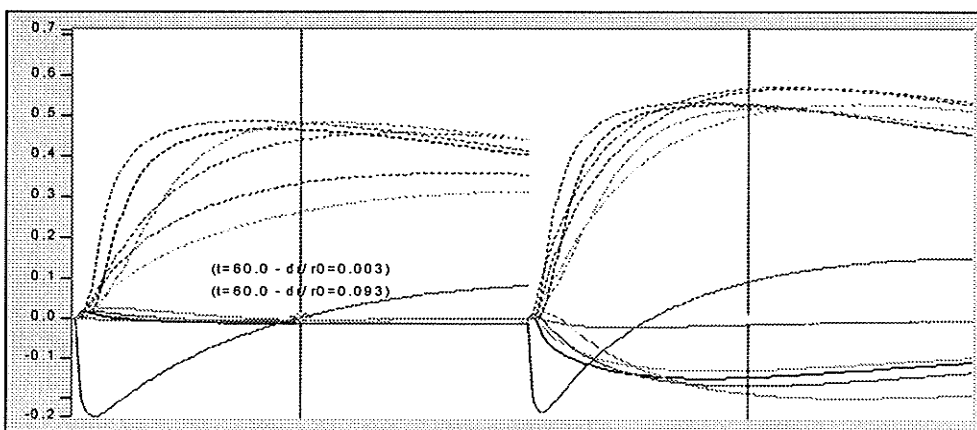
7a. Wool Challis – unexposed and exposed – incubated at 35°C



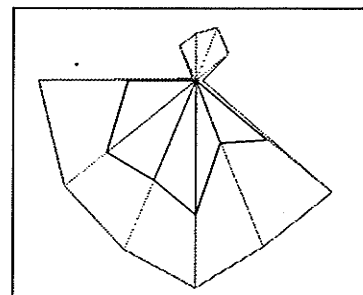
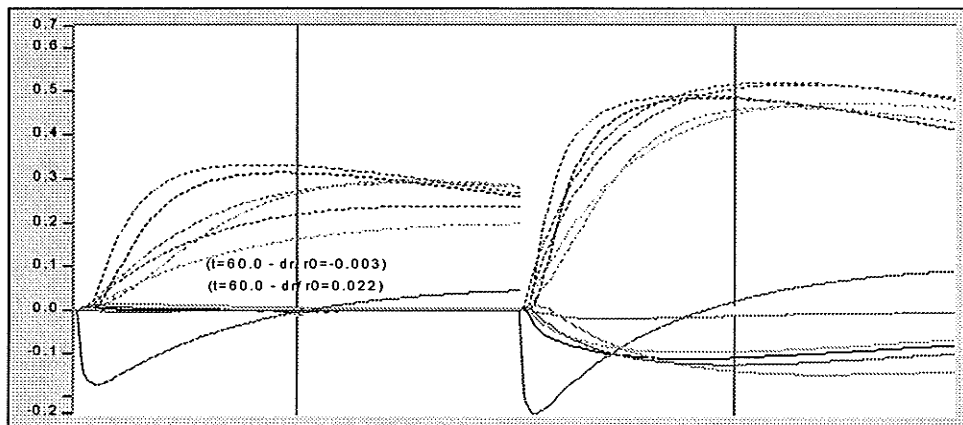
7b. Wool Challis – unexposed and exposed – incubated at 40°C



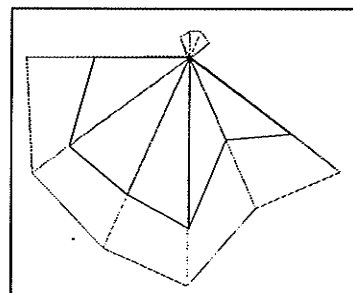
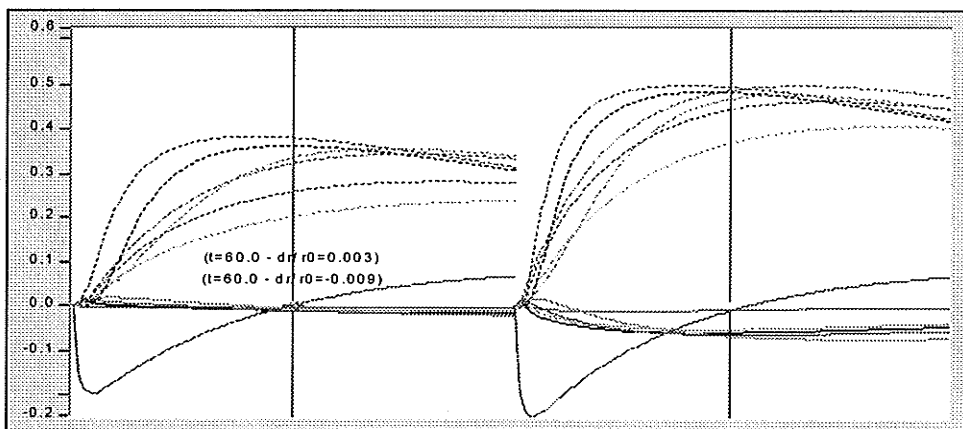
7c. Wool Challis – unexposed and exposed – incubated at 60°C



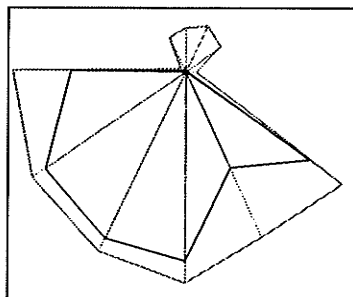
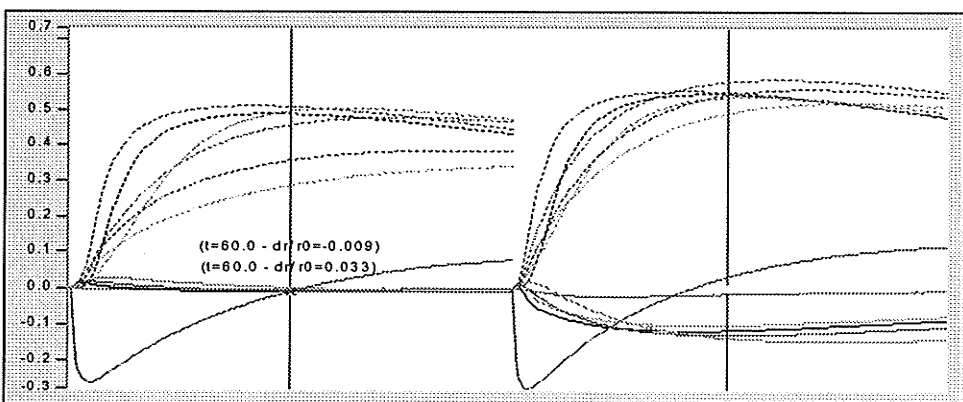
8a. Silk Habutae – unexposed and exposed – incubated at 35°C



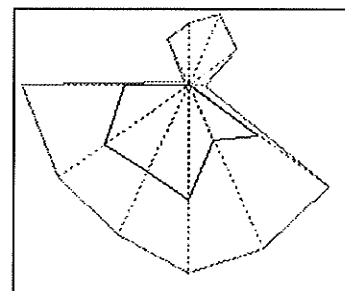
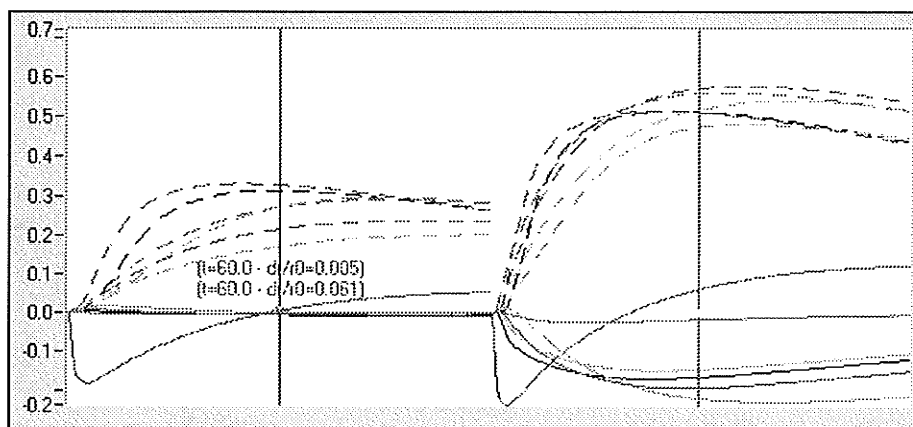
8b. Silk Habutae – unexposed and exposed – incubated at 40°C



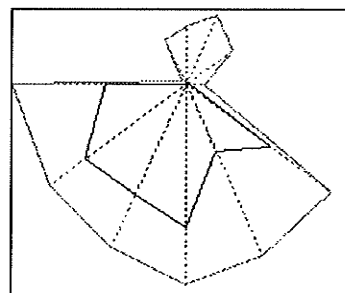
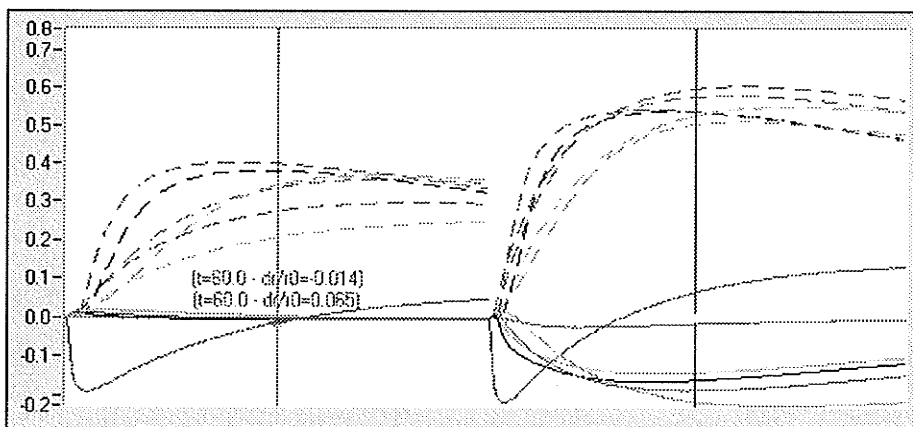
8c. Silk Habutae – unexposed and exposed – incubated at 60°C



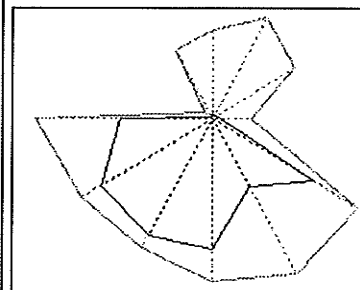
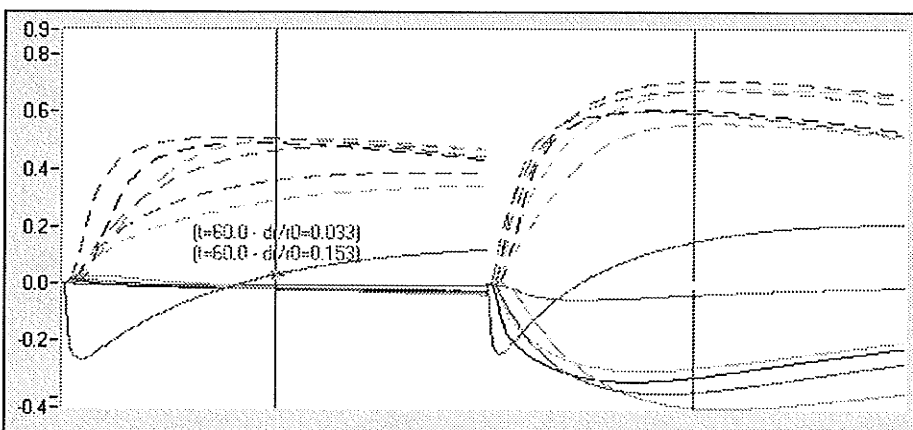
9a. Linen – unexposed and exposed – incubated at 35°C



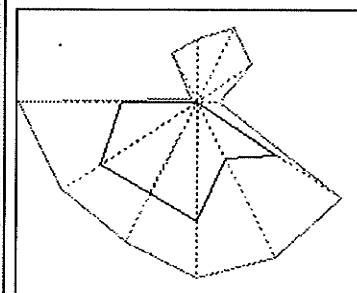
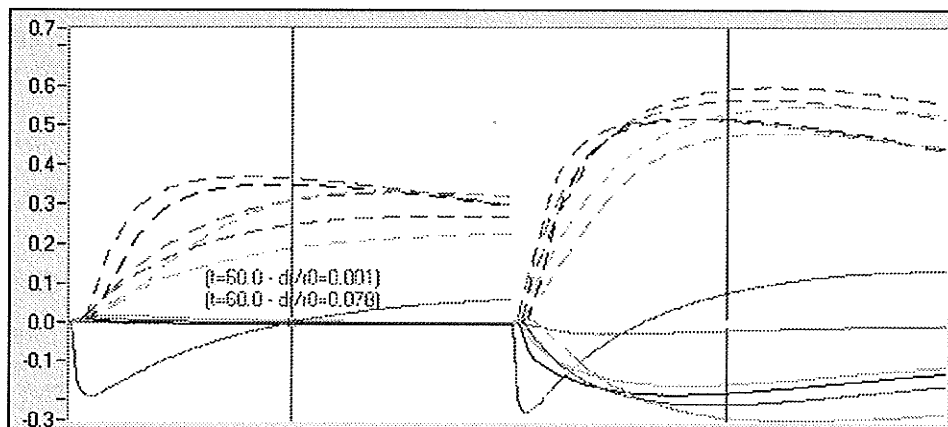
9b. Linen – unexposed and exposed – incubated at 40°C



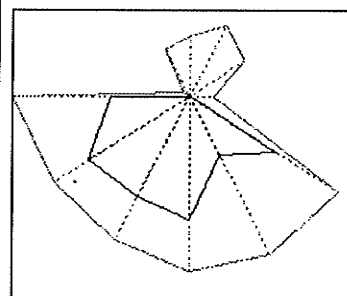
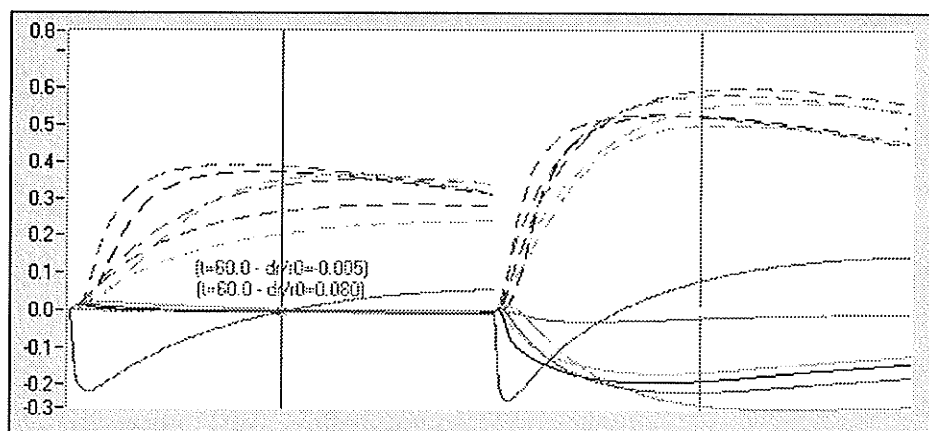
9c. Linen – unexposed and exposed – incubated at 60°C



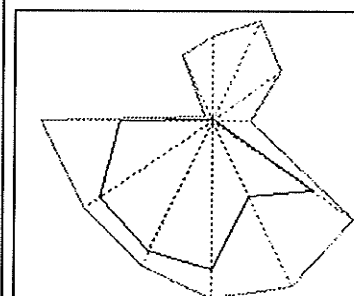
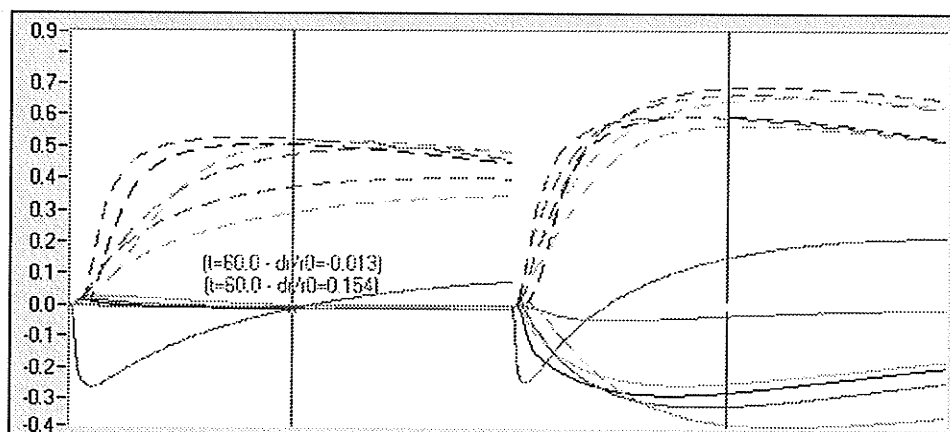
10a. Spun viscose challis (rayon) – unexposed and exposed – incubated at 35°C



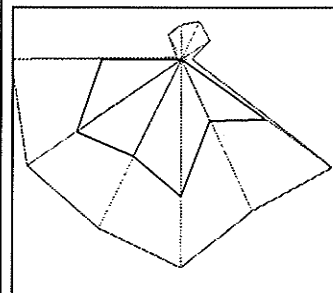
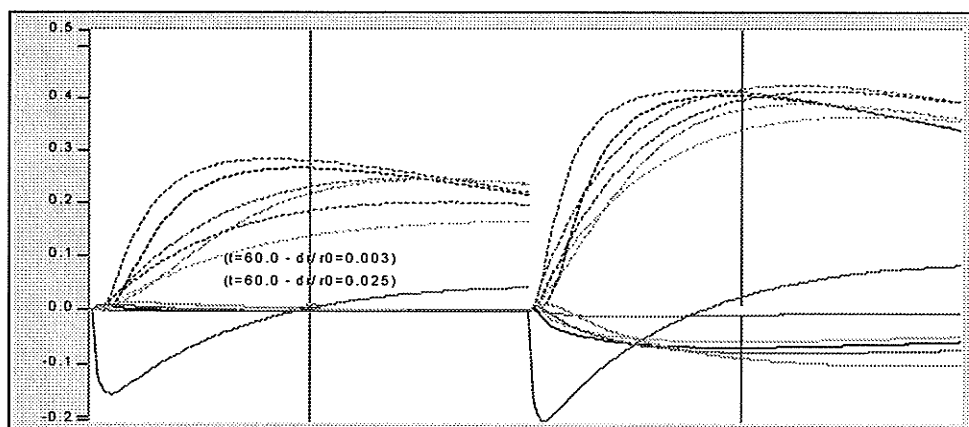
10b. Spun viscose challis (rayon) – unexposed and exposed – incubated at 40°C



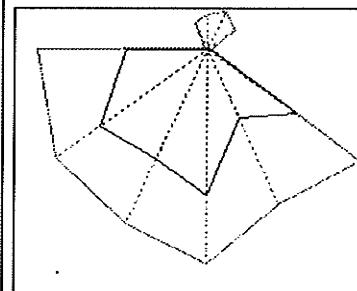
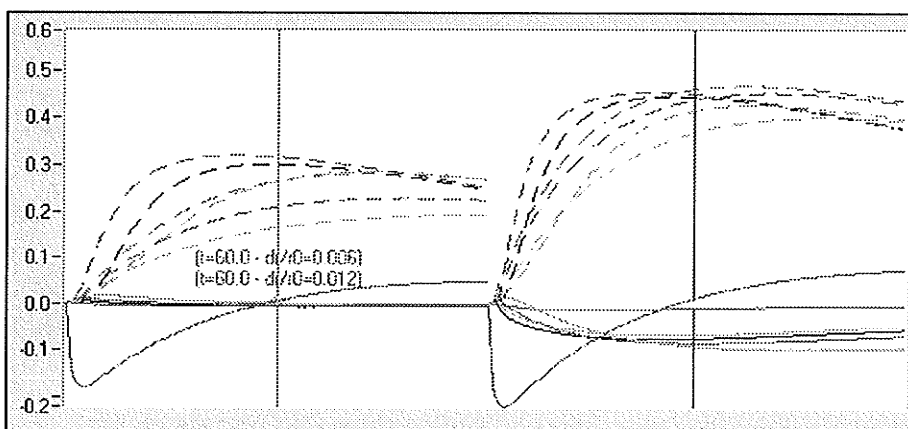
10c. Spun viscose challis (rayon) – unexposed and exposed – incubated at 60°C



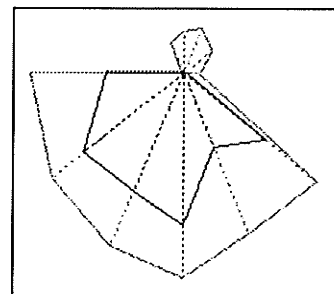
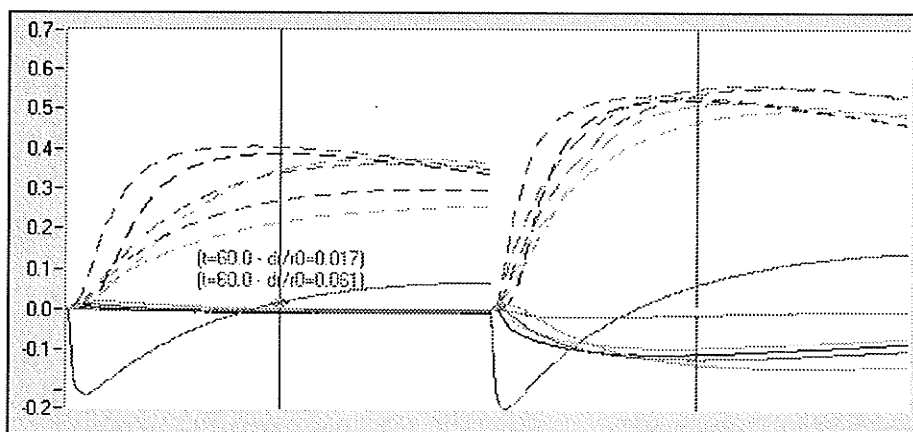
11a. Dacron type 54 – unexposed and exposed incubated at 35°C



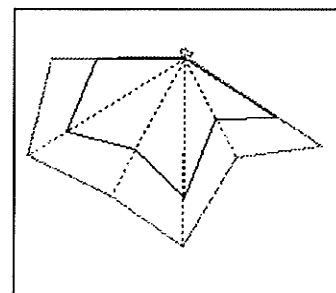
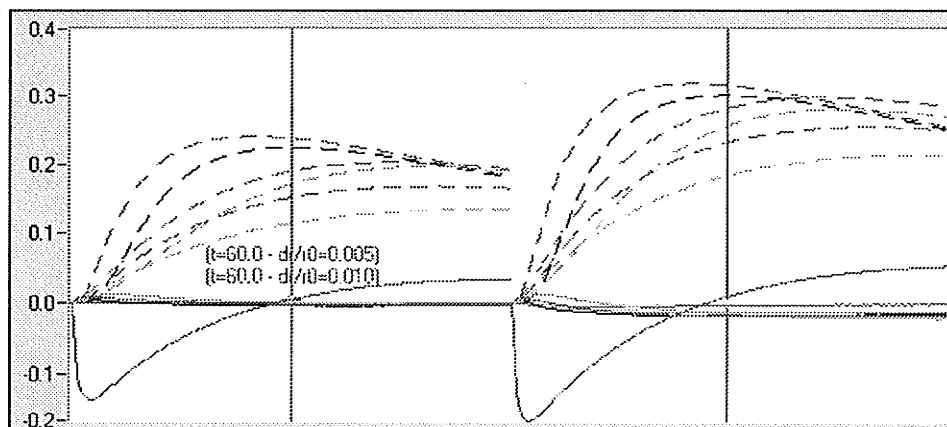
11b. Dacron type 54 – unexposed and exposed incubated at 40°C



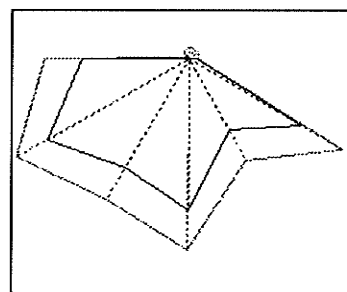
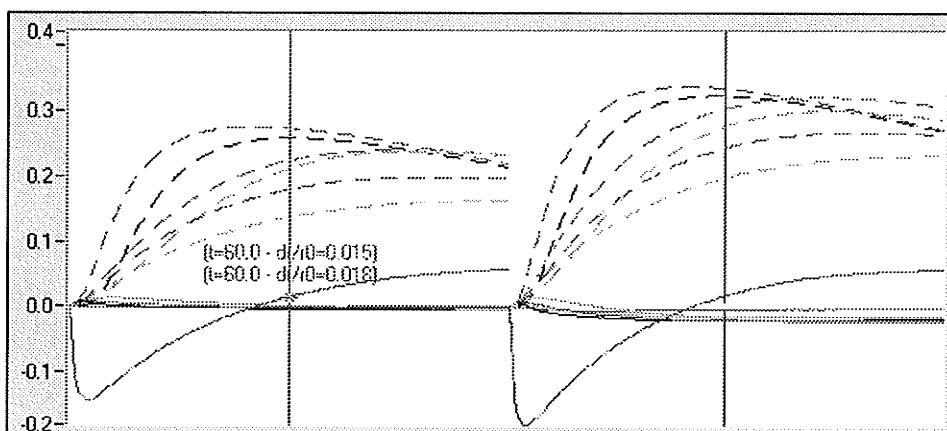
11c. Dacron type 54 – unexposed and exposed incubated at 60°C



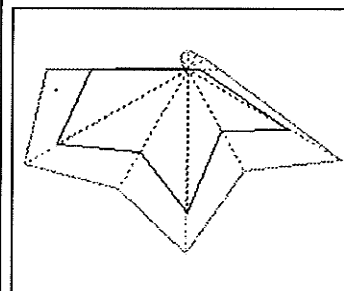
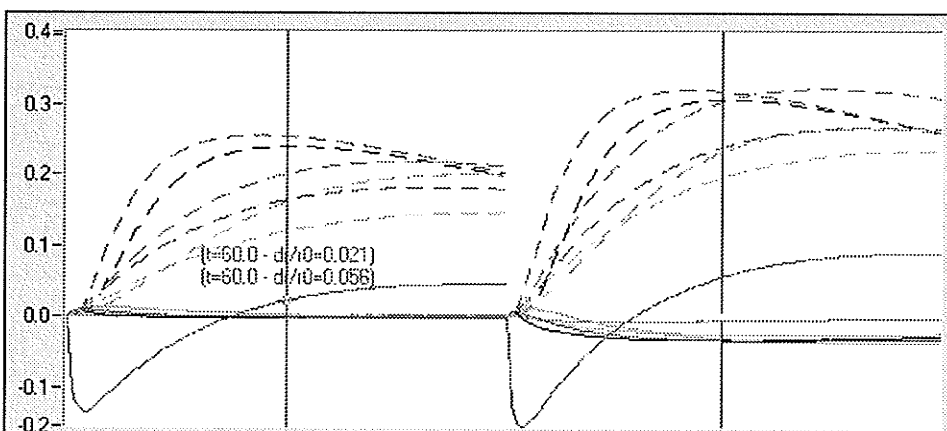
12a. Spun polypropylene – unexposed and exposed – incubated at 35°C



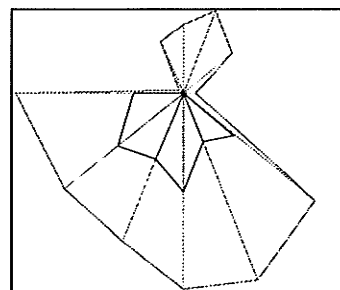
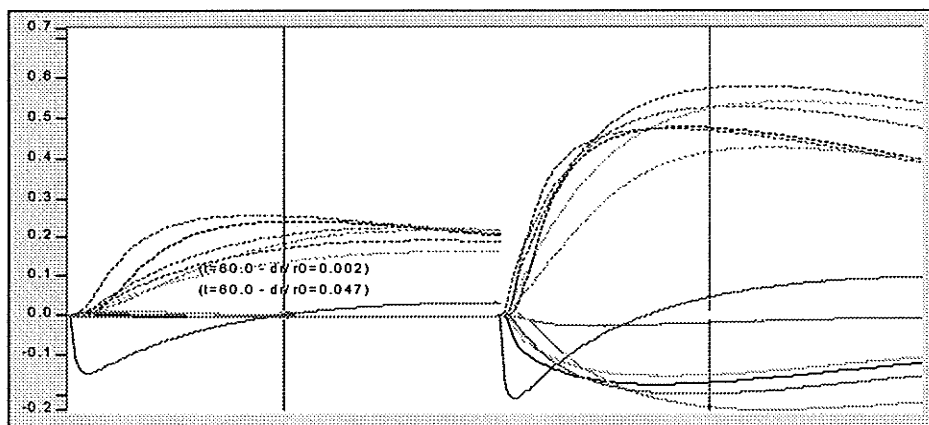
12b. Spun polypropylene – unexposed and exposed – incubated at 40°C



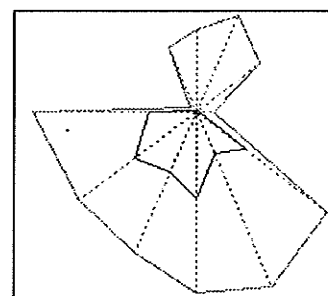
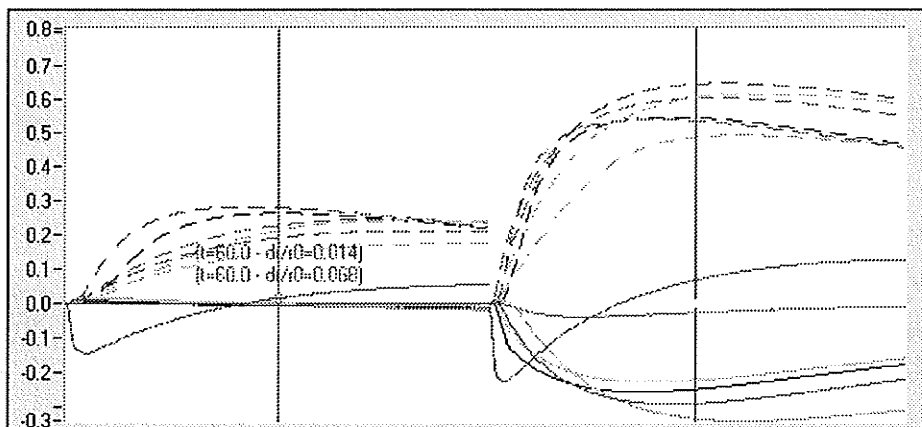
12c. Spun polypropylene – unexposed and exposed – incubated at 60°C



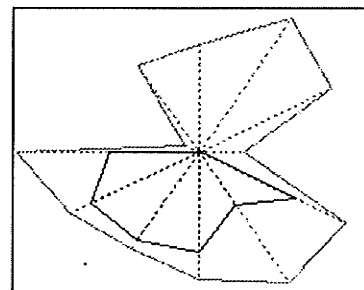
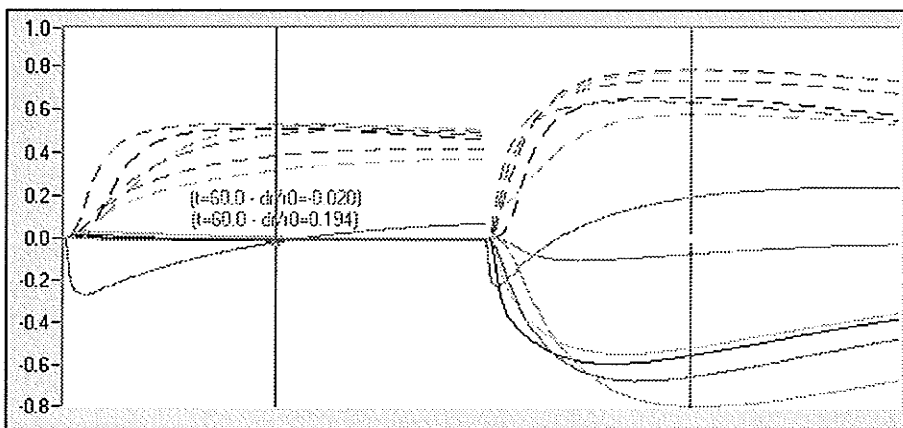
13a. Activated Carbon Cloth - Unexposed and Exposed (Exposed) - incubated at 35°C



13b. Activated Carbon Cloth - Unexposed and Exposed - incubated at 40°C



13c. Activated Carbon Cloth - Unexposed and Exposed - incubated at 60°C



Appendix I

Principal component analysis (PCA) graphs

comparing unexposed and exposed samples for each of the thirteen cloth swatches tested.

Principal component analysis (PCA) graphs of the electronic nose response data to show the detection of differences in odor level between unexposed and exposed samples for each of the 13 cloth samples tested.

The following table shows the cloth sample tested and the figure in which it appears in this section.

Sample Code for the Electronic Nose Analysis	Fabric Description	Figure Number in this Section	
COT	cotton - flannel, bleached	I.1.	
	two further sets of cotton flannel analyzed separately	I.14	I.15
CTB	cotton broadcloth, bleached, mercerized, combed	I.2.	
CTK	cotton - knit - bleached cotton t-shirt fabric	I.3.	
CTT	cotton - 9.5 oz, bleached terry cloth	I.4.	
CTW	cotton - twill, bleached, mercerized	I.5.	
WOL	wool - worsted flannel	I.6.	
WLC	wool challis	I.7.	
SLK	silk habutae 8 mm	I.8.	
LIN	linen - suiting	I.9.	
RAY	spun viscose challis (rayon)	I.10.	
DAC	Dacron type 54 (disperse dyeable)	I.11.	
PLY	spun polypropylene	I.12.	
ACC	activated carbon cloth	I.13.	

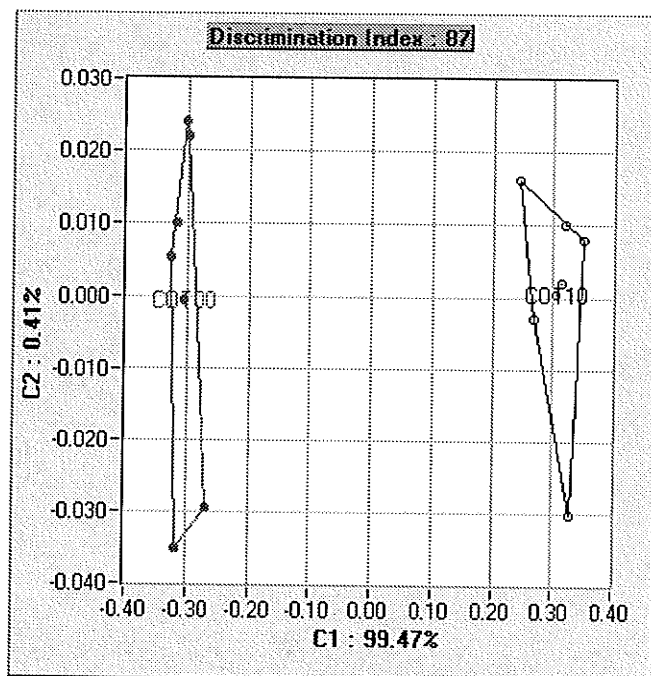


Figure I.1. PCA graph for the cotton flannel samples (COT).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 87% indicating a clear discrimination between the two groups of samples.

The data in this graphs represents samples prepared and tested on two different days and includes 6 data points for each of the samples instead of the three used for each of the subsequent fabric samples.

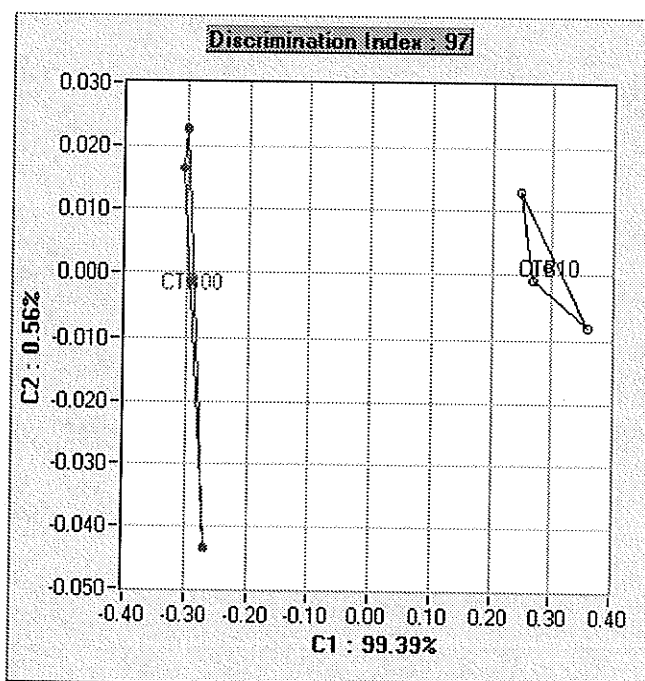


Figure I.2. PCA graph for the cotton broadcloth samples (CTB).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 97% indicating a clear discrimination between the two groups of samples.

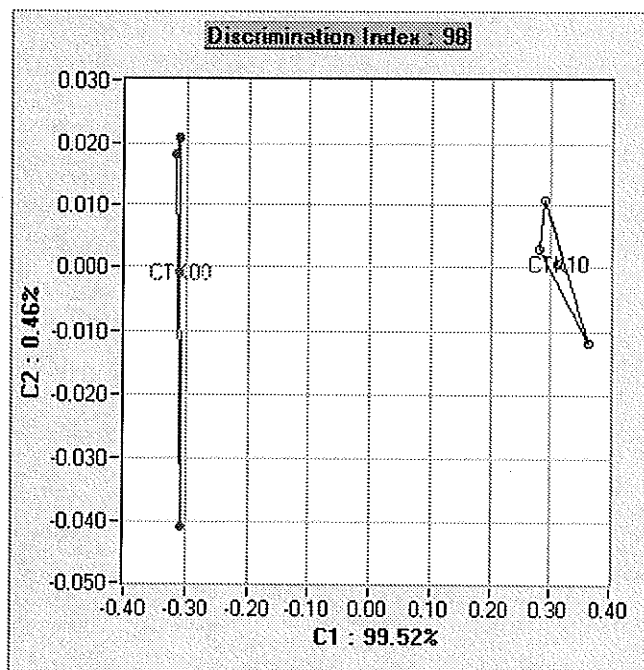


Figure I.3. PCA graph for the cotton knit samples (CTK).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 98% indicating a clear discrimination between the two groups of samples.

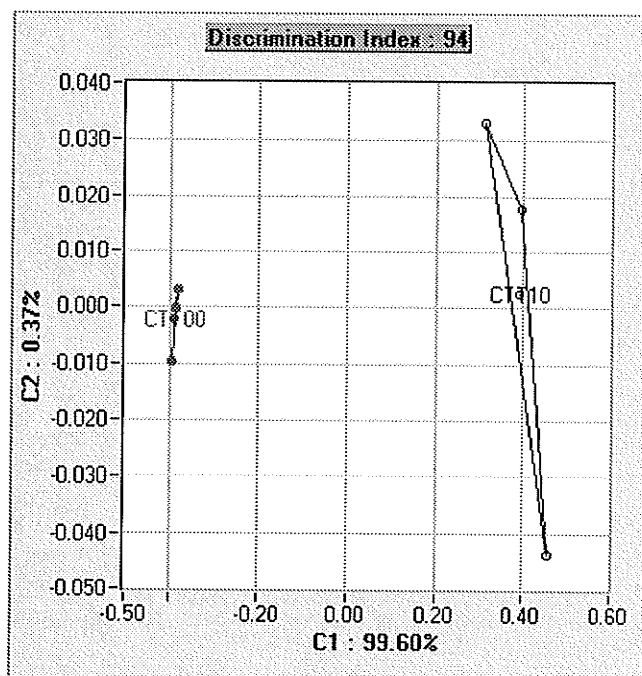


Figure I.4. PCA graph for the cotton terry cloth samples (CTT). There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 94% indicating a clear discrimination between the two groups of samples.

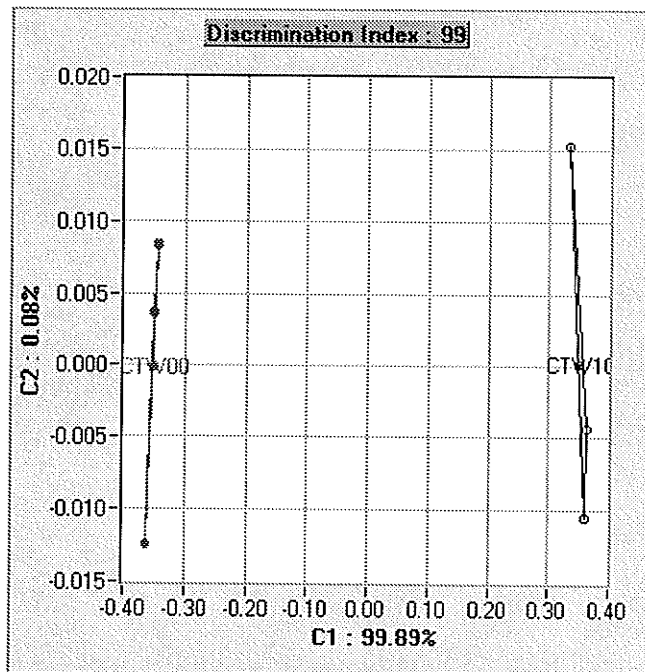


Figure I.5. PCA graph for the cotton twill samples (CTW).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 99% indicating a clear discrimination between the two groups of samples.

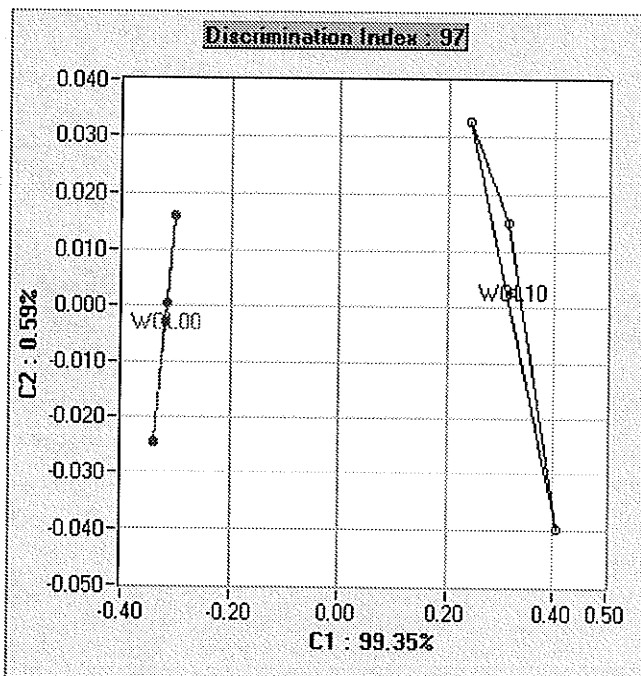


Figure I.6. PCA graph for the wool flannel samples ((WOL).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 97% indicating a clear discrimination between the two groups of samples.

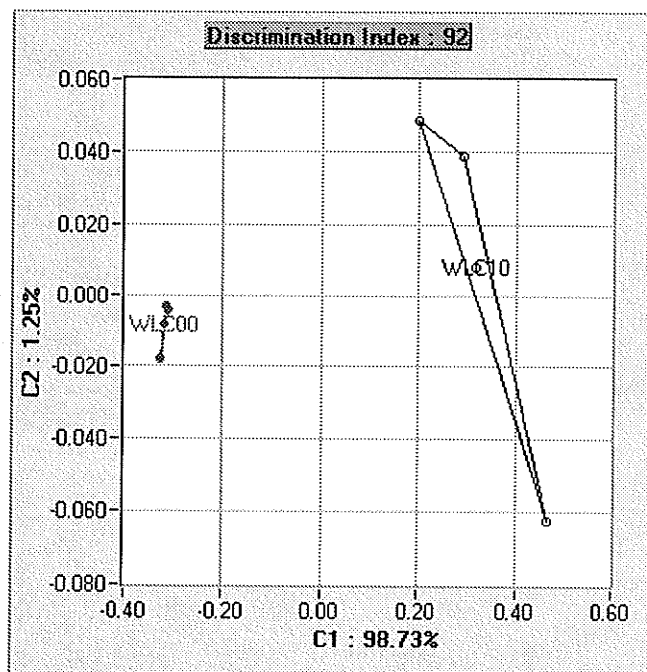


Figure I.7. PCA graph for the wool challis samples (WLC).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 92% indicating a clear discrimination between the two groups of samples.

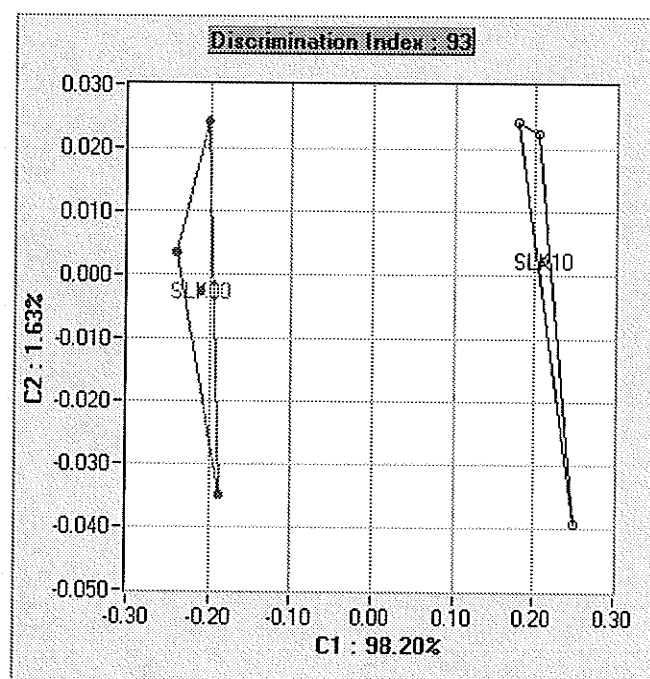


Figure I.8. PCA graph for the silk habutae samples (SLK).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 93% indicating a clear discrimination between the two groups of samples.

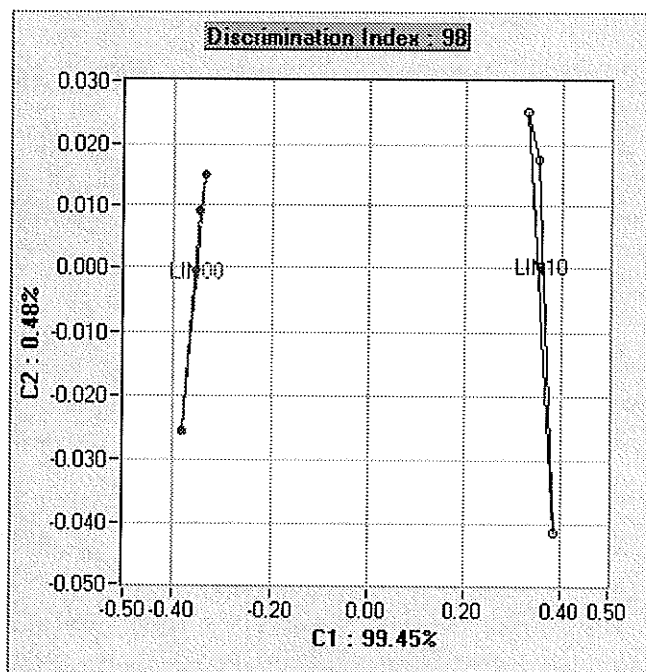


Figure I.9. PCA graph for the linen suiting samples (LIN).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 98% indicating a clear discrimination between the two groups of samples.

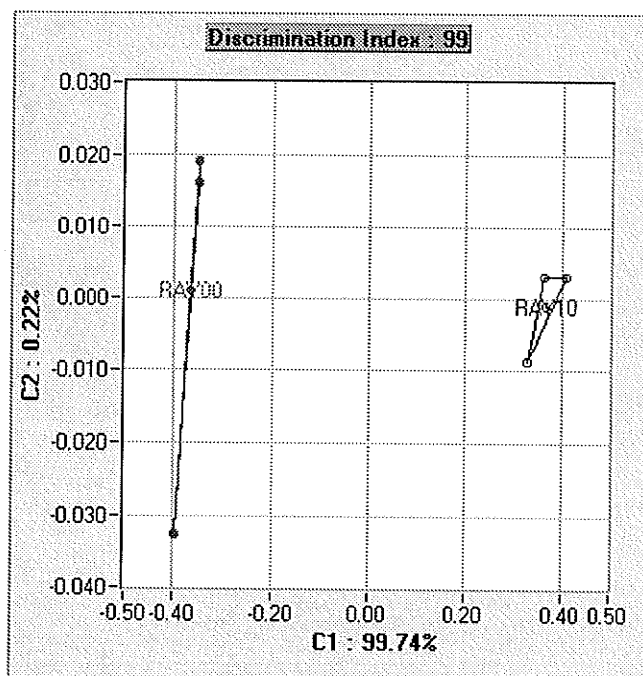


Figure I.10. PCA graph for the spun viscose challis - rayon samples (RAY).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 99% indicating a clear discrimination between the two groups of samples.

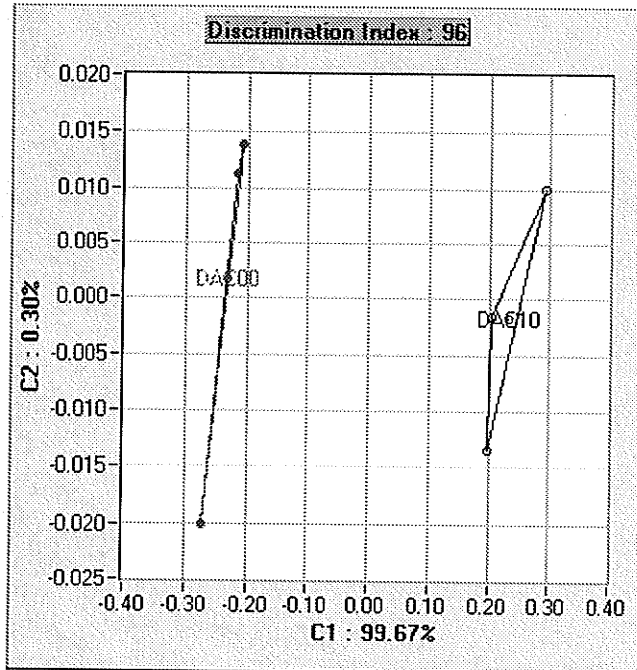


Figure I.11. PCA graph for the Dacron type 54 samples (DAC).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 96% indicating a clear discrimination between the two groups of samples.

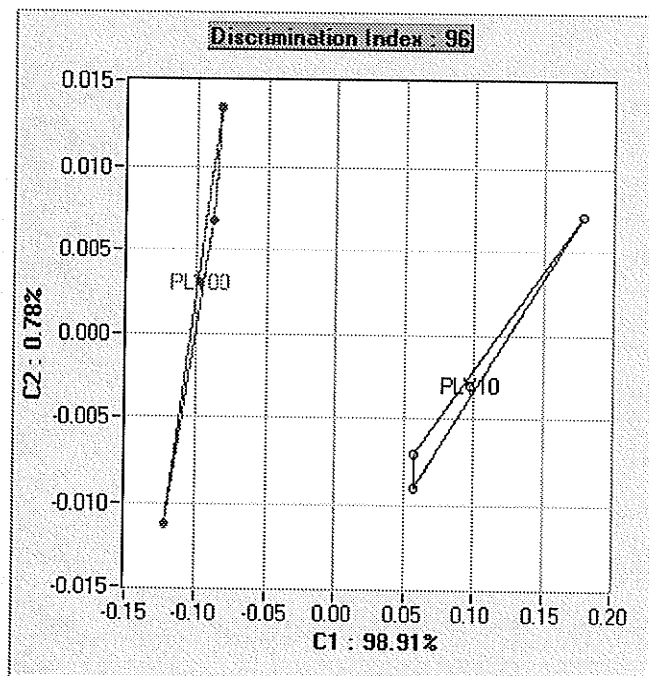


Figure I.12. PCA graph for the spun polypropylene samples (PLY).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 96% indicating a clear discrimination between the two groups of samples.

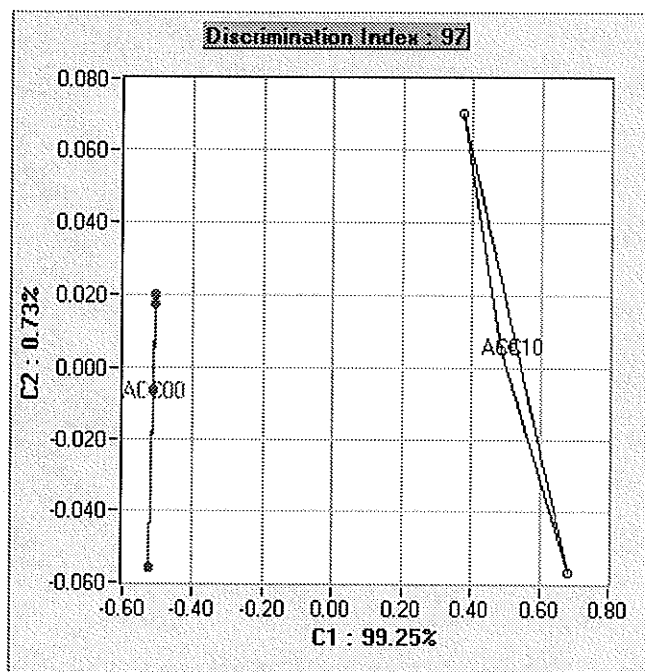


Figure I.13. PCA graph for the activated carbon cloth samples (ACC).

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 97% indicating a clear discrimination between the two groups of samples.

Two further sets of cotton flannel samples mapped separately to demonstrate the stability of the effect and the range of discrimination indices which were found in this testing

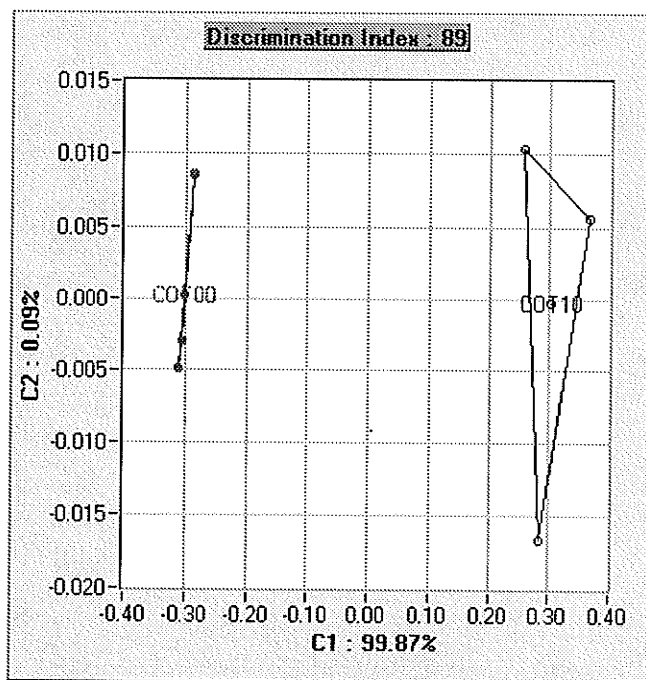


Figure I.14 PCA graph for the cotton flannel samples (COT). From October 9.

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 89% indicating a clear discrimination between the two groups of samples.

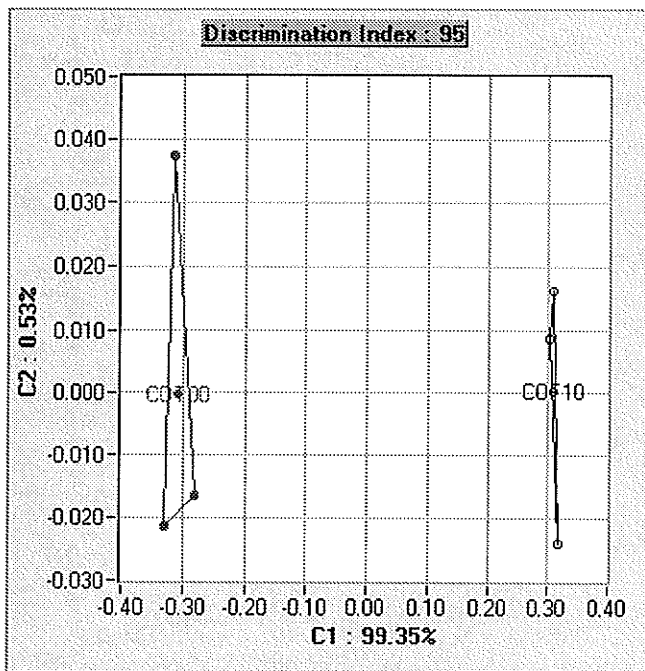


Figure I.15. PCA graph for the cotton flannel samples (COT) from October 10.

There is a clear difference between the untreated (00) sample and the exposed (10) sample. The discrimination index is 95% indicating a clear discrimination between the two groups of samples.

There is some variation between the samples from day to day – the proximity in time makes it unlikely that the changes will be due to changes in the

Appendix J

Ballot and instructions used for the collection of environmental malodor intensity data for swine odors during the odor dispersion study.

ODOUR INTENSITY DATA RECORDING FORM - FOR SESSION 2 _____

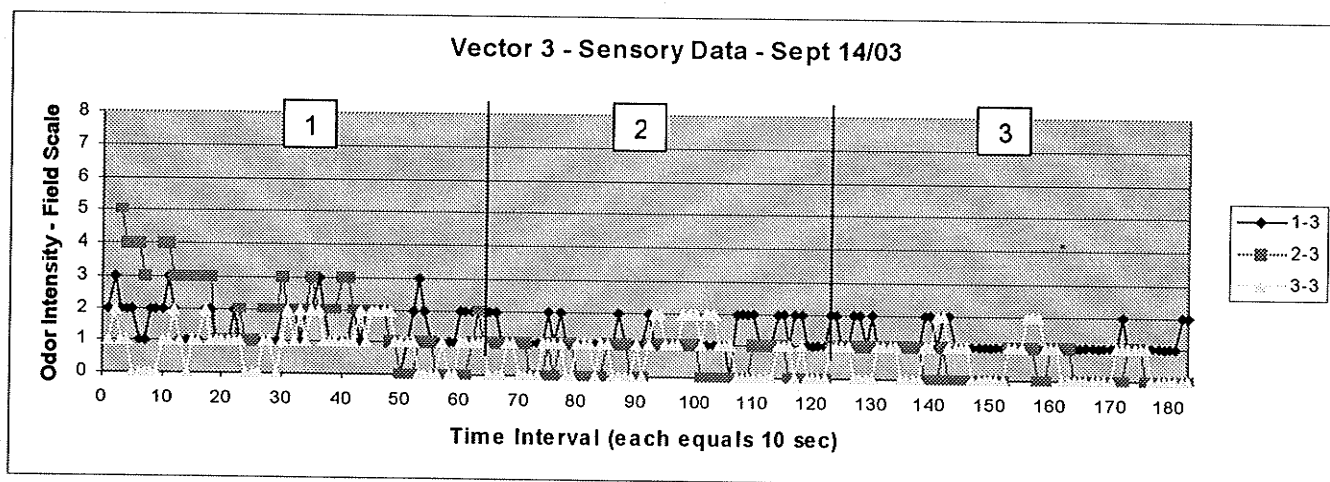
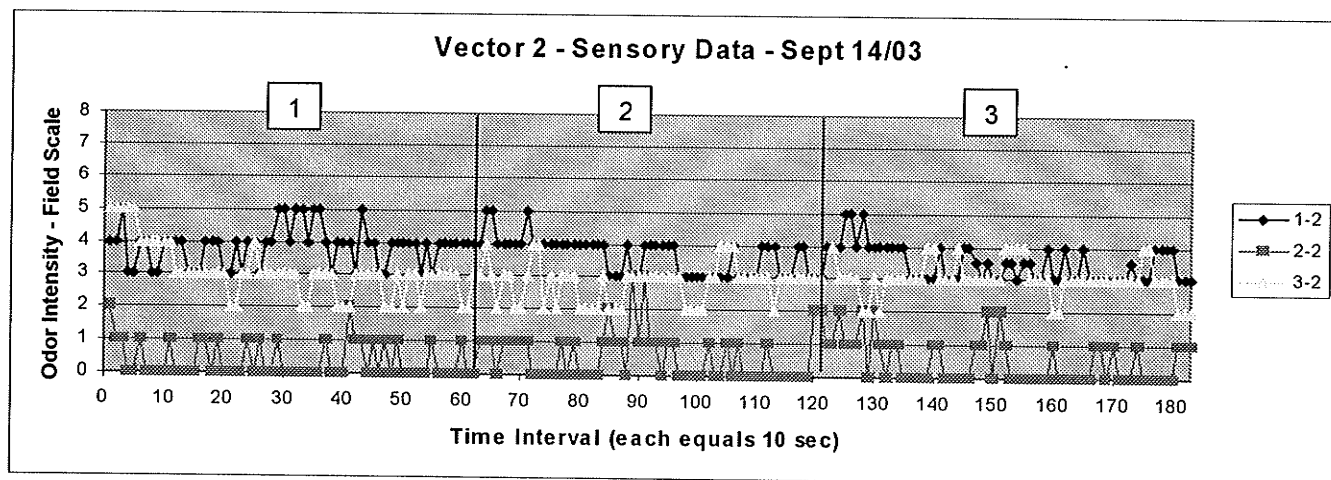
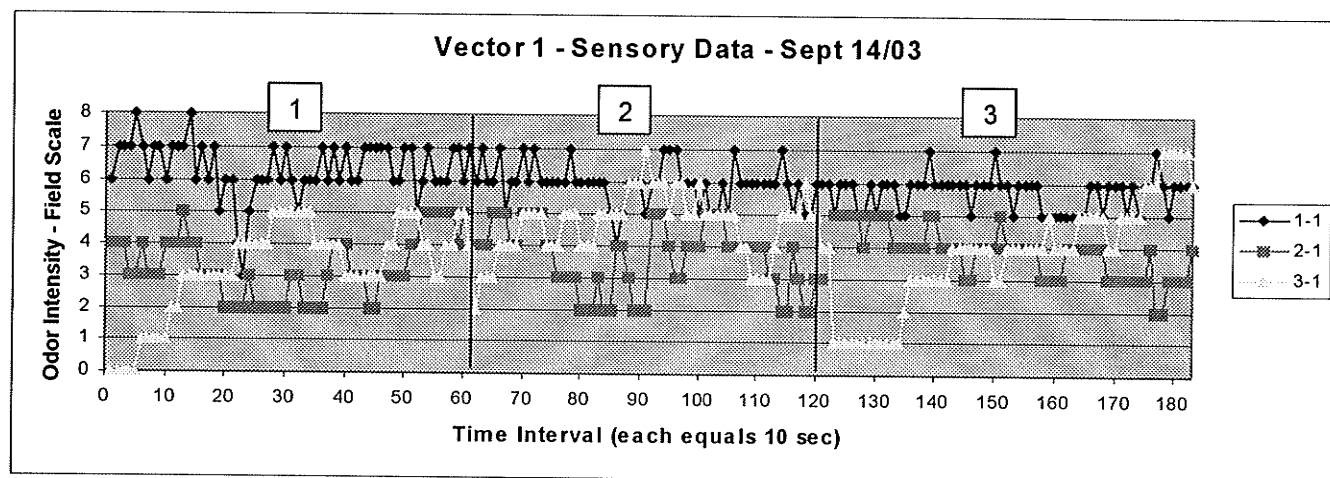
Sniffer _____		Date _____		Position 2 – 2	
Sequence # 2		GPS Position:			
		Longitude: _____		Latitude: _____	
Instructions: 1. Put mask in place and move to field position. Record GPS position above. 2. On signal or at agreed time, begin data collection for sequence 1: • remove mask for 1-2 sec, sniff air, replace mask • record odor intensity and any descriptors appropriate.....repeat these steps for 10 min. 3. Wait 10 minutes until next signal to do sequence 2 and then sequence 3.					
Time	Standard sample scale (circle the number of the standard closest in intensity to the air sample)	Odor Descriptor	Comments (e.g. non-swine odors)		
at 0 min	0 1 2 3 4 5 6 7 8				
10 sec	0 1 2 3 4 5 6 7 8				
20 sec	0 1 2 3 4 5 6 7 8				
30 sec	0 1 2 3 4 5 6 7 8				
40 sec	0 1 2 3 4 5 6 7 8				
50 sec	0 1 2 3 4 5 6 7 8				
at 1 min	0 1 2 3 4 5 6 7 8				
10 sec	0 1 2 3 4 5 6 7 8				
20 sec	0 1 2 3 4 5 6 7 8				
30 sec	0 1 2 3 4 5 6 7 8				
40 sec	0 1 2 3 4 5 6 7 8				
50 sec	0 1 2 3 4 5 6 7 8				
at 2 min	0 1 2 3 4 5 6 7 8				
10 sec	0 1 2 3 4 5 6 7 8				
20 sec	0 1 2 3 4 5 6 7 8				
30 sec	0 1 2 3 4 5 6 7 8				
40 sec	0 1 2 3 4 5 6 7 8				
50 sec	0 1 2 3 4 5 6 7 8				
at 3 min	0 1 2 3 4 5 6 7 8				
10 sec	0 1 2 3 4 5 6 7 8				
20 sec	0 1 2 3 4 5 6 7 8				
30 sec	0 1 2 3 4 5 6 7 8				
40 sec	0 1 2 3 4 5 6 7 8				
50 sec	0 1 2 3 4 5 6 7 8				
at 4 min	0 1 2 3 4 5 6 7 8				
10 sec	0 1 2 3 4 5 6 7 8				
20 sec	0 1 2 3 4 5 6 7 8				
30 sec	0 1 2 3 4 5 6 7 8				
40 sec	0 1 2 3 4 5 6 7 8				
50 sec	0 1 2 3 4 5 6 7 8				

Odour Descriptors:	1) acrid/pungent 2) ammonia 3) chopped hay 4) earthy 5) fecal – human	6) fecal – animal 7) fresh manure 8) old manure 9) moldy/musty 10) putrid/rotten flesh	11) rotten eggs 12) sewage 13) smoky 14) sulphur 15) sweetish
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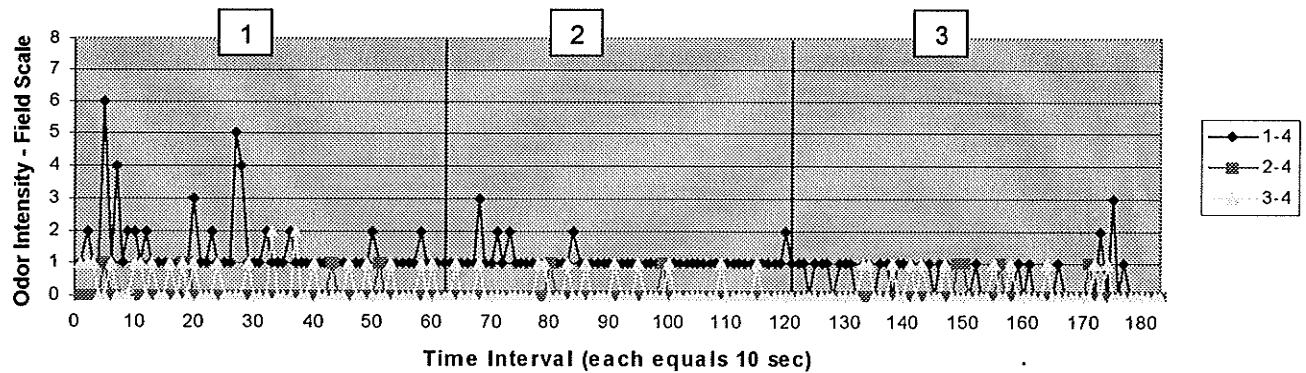
Appendix K

Vector graphs for odor response data over three consecutive 10-minute periods
for the three days of field testing.

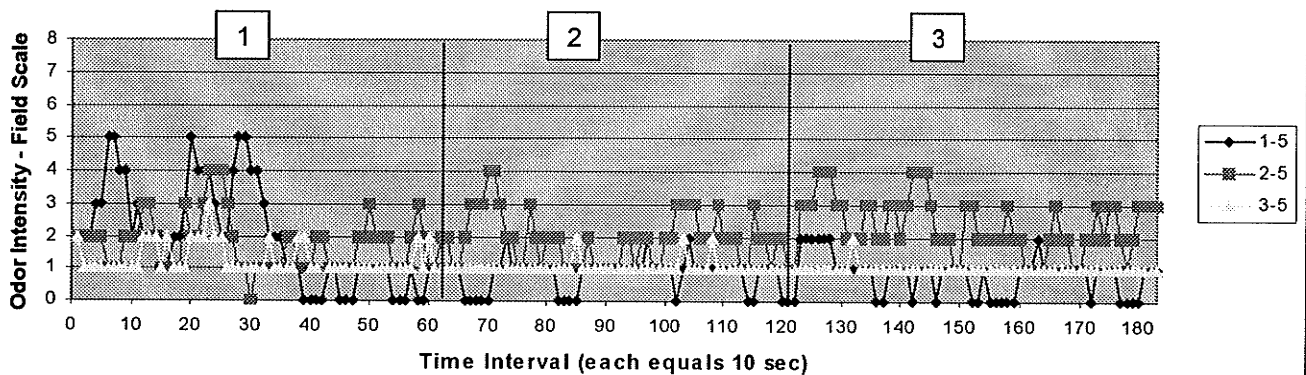
Figure K.1. Vector graphs of the odor plumes from September 14, 2003. These show the variations in the odor for the three 10 minute sampling periods Start time: 11.00 Temperature 13.7°C, R.H. 82.8%, and wind-speed 11.1 km/hr.



Vector 4 - Sensory Data - Sept 14/03



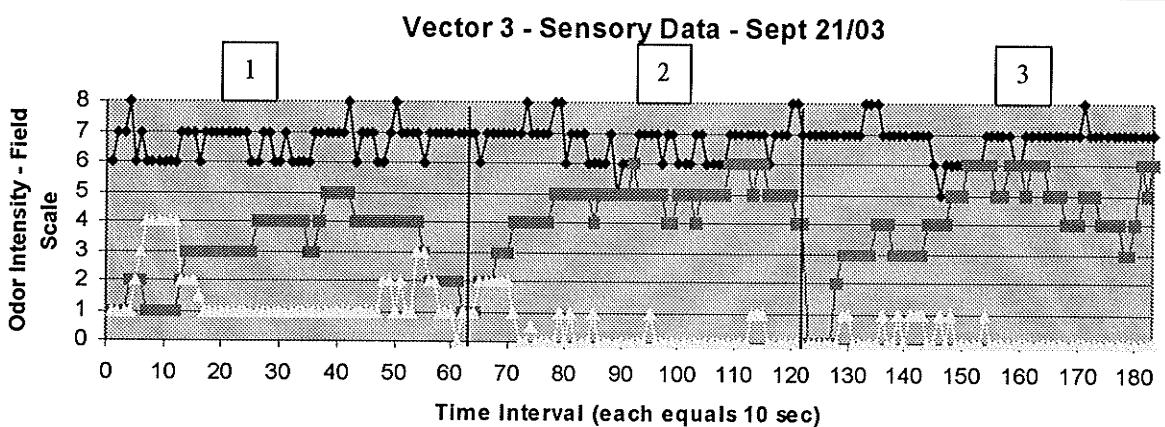
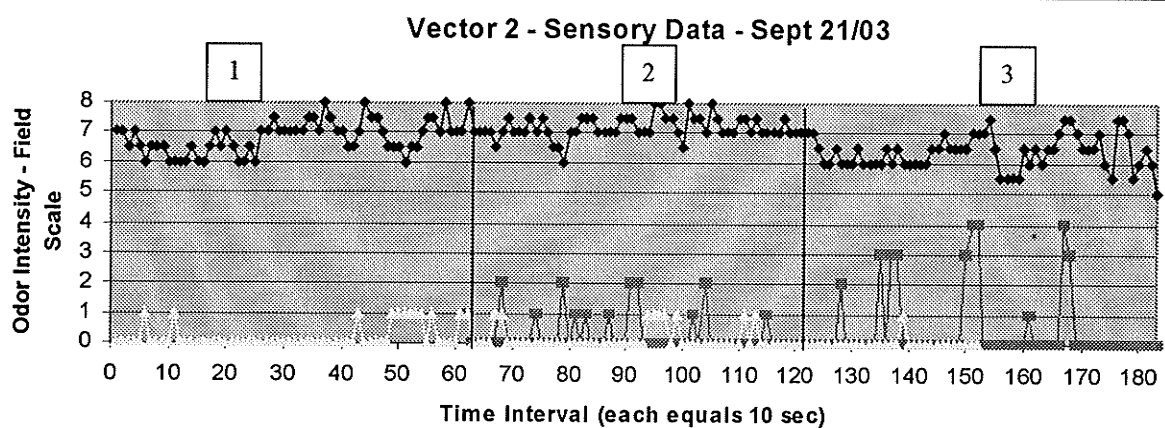
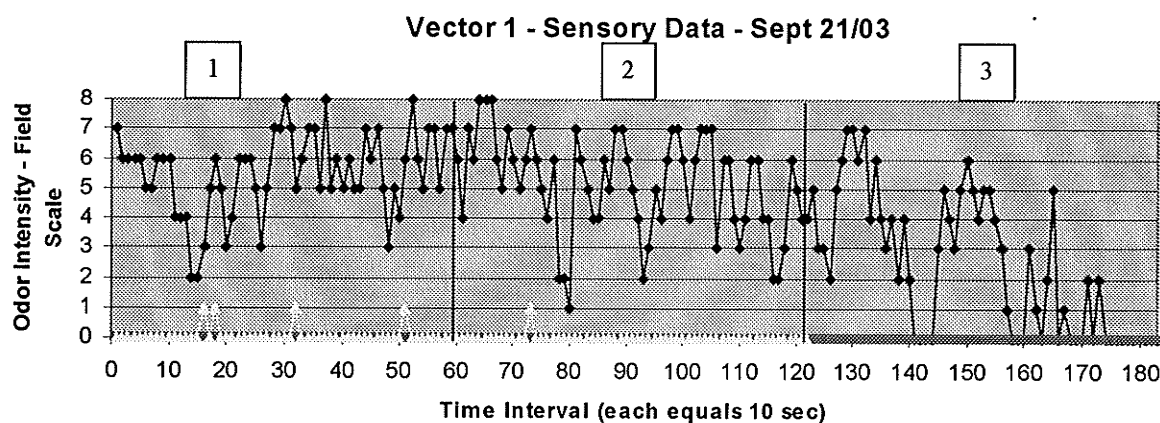
Vector 5 - Sensory Data - Sept 14/03

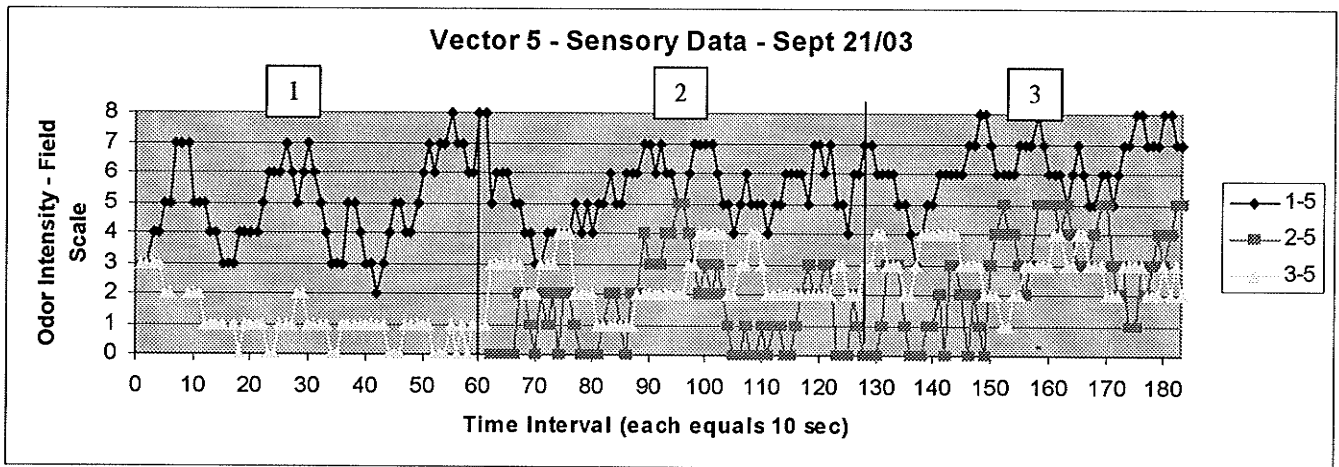
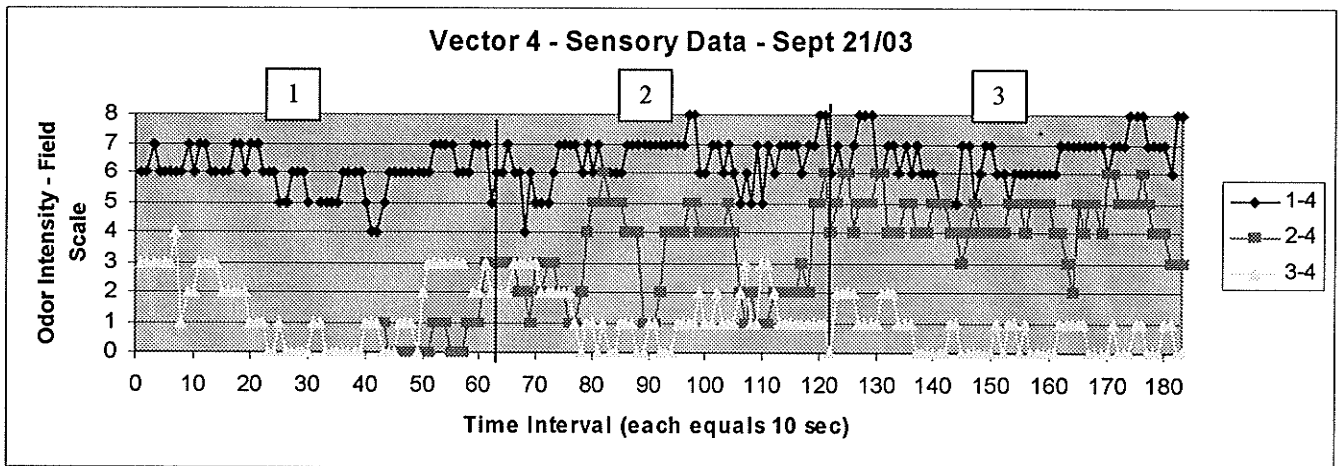


Note: each of the three lines is interpreted as follows:

- 1-(vector number) is position 1 on that vector = 100 m from the odor source.
- 2-(vector number) is position 1 on that vector = 500 m from the odor source.
- 3-(vector number) is position 1 on that vector = 1000 m from the odor source.

Figure K.2. Vector graphs of the odor plumes from September 21, 2003. These show the variations in the odor for the three 10 minute sampling periods Start time: 15.10 Temperature 11.0°C, R.H. 92.2%, and wind-speed 21.7 km/hr.





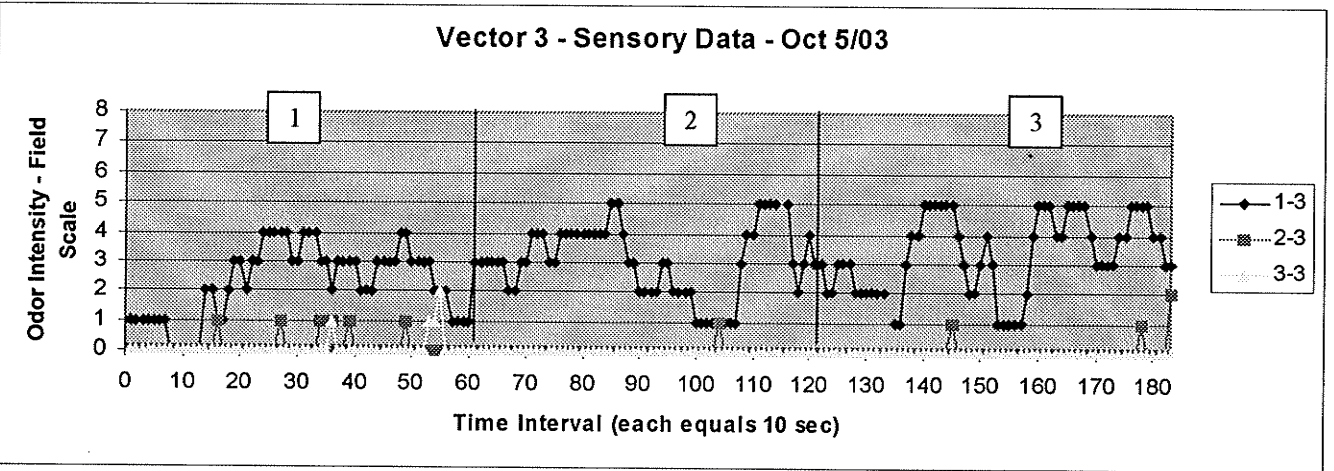
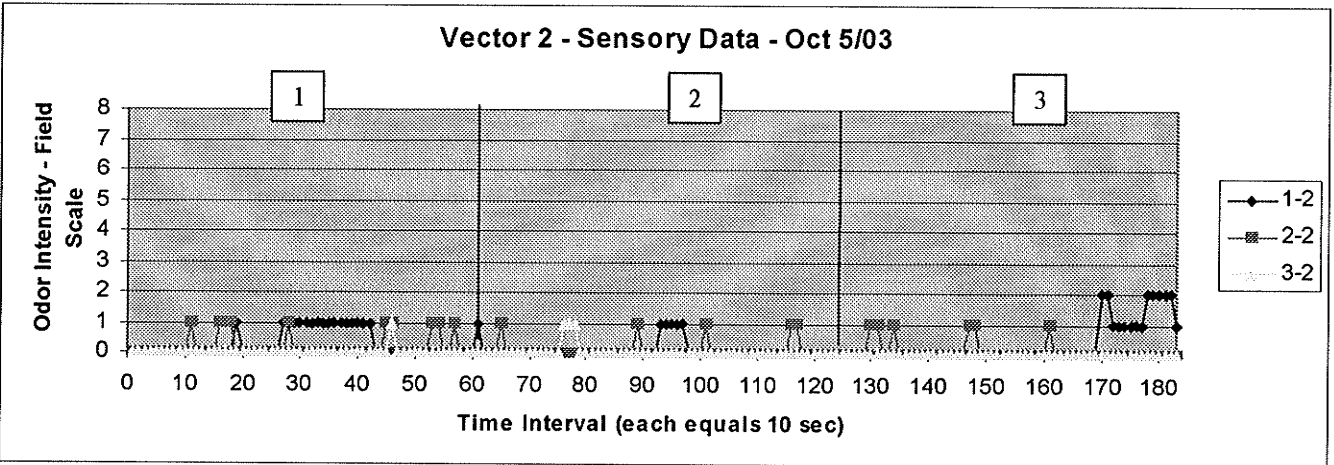
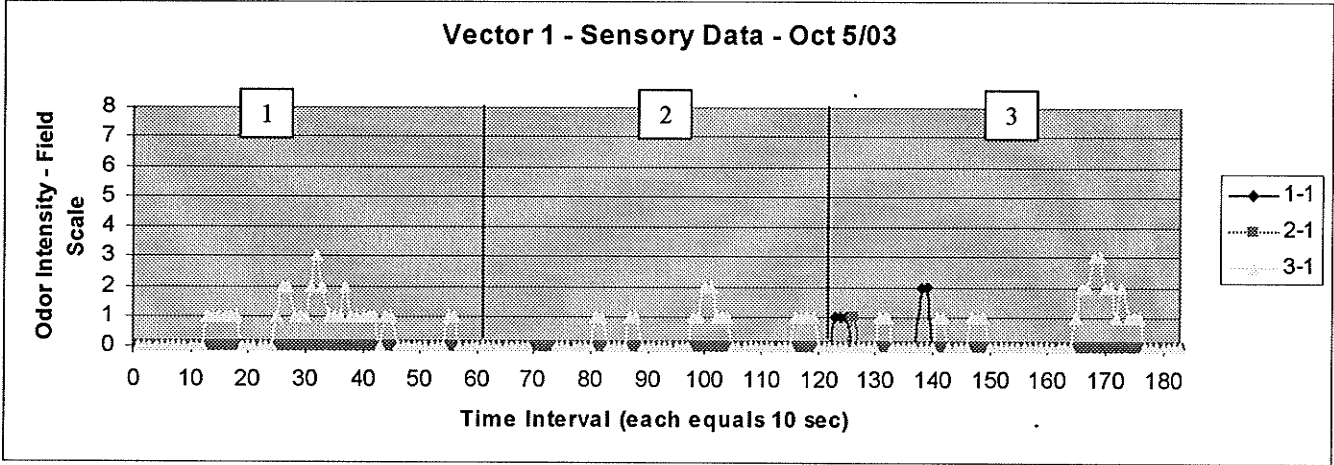
Note: each of the three lines is interpreted as follows:

1-(vector number) is position 1 on that vector = 100 m from the odor source.

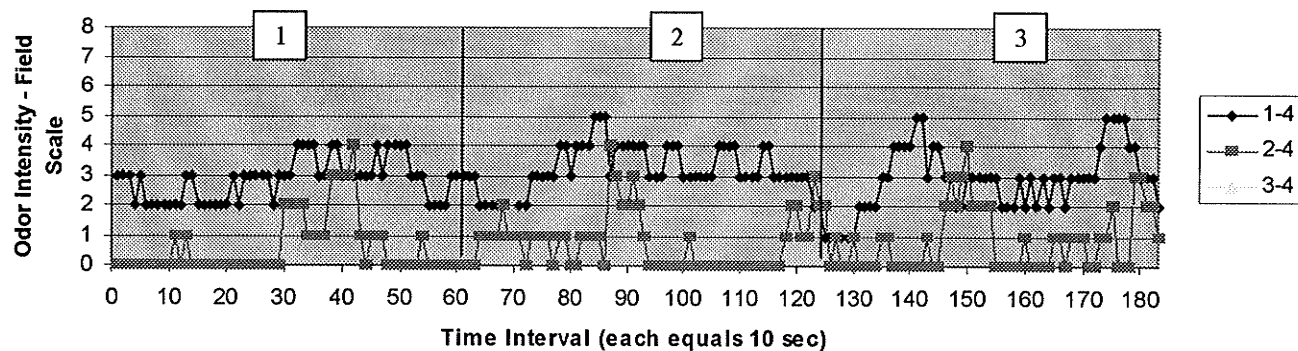
2-(vector number) is position 1 on that vector = 500 m from the odor source.

3-(vector number) is position 1 on that vector = 1000 m from the odor source.

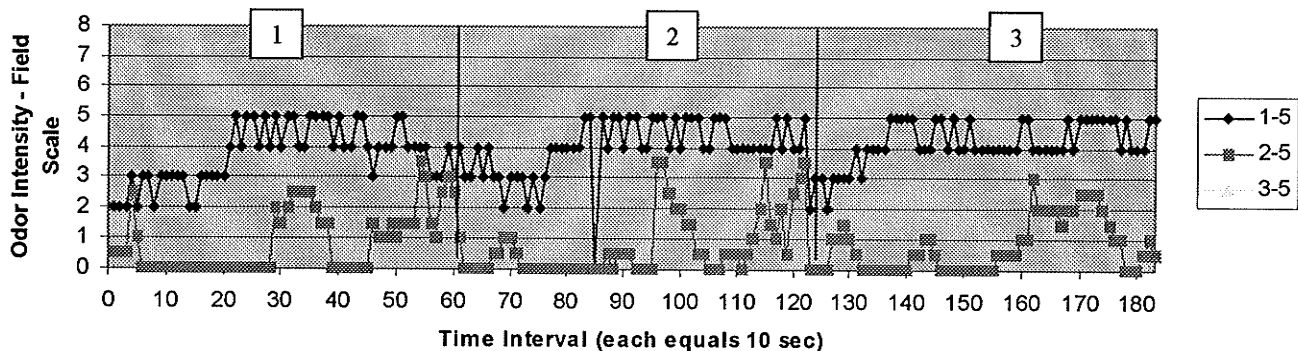
Figure K.3. Vector graphs of the odor plumes from October 5, 2003. These show the variations in the odor for the three 10 minute sampling periods Start time: 12.01 Temperature 15.1°C, R.H. 51.7%, and wind-speed 15.8 km/hr.



Vector 4 - Sensory Data - Oct 5/03



Vector 5 - Sensory Data - Oct 5/03



Note: each of the three lines is interpreted as follows:

- 1-(vector number) is position 1 on that vector = 100 m from the odor source.
- 2-(vector number) is position 1 on that vector = 500 m from the odor source.
- 3-(vector number) is position 1 on that vector = 1000 m from the odor source.

Appendix L.

ESCA curves for the analysis of the surface composition of the fabrics tested.

The following ESCA curves were supplied by S. Turgeon, Universitaire de Québec, Hôpital Saint-François d'Assise, Québec, Canada.

- Figure L.1. (a), (b) and (c) ESCA curves for COT
- Figure L.2. (a), (b) and (c) ESCA curves for CO₂
- Figure L.3. (a), (b) and (c) ESCA curves for C_F
- Figure L.4. (a), (b) and (c) ESCA curves for PLY
- Figure L.5. (a), (b) and (c) ESCA curves for PO₂
- Figure L.6. (a), (b) and (c) ESCA curves for P_F

4i14st1.spe: ech, M. King: cotton-control, 1
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Ful/1

2.4118e+004 max

UBB/CRSFA
6.42 min

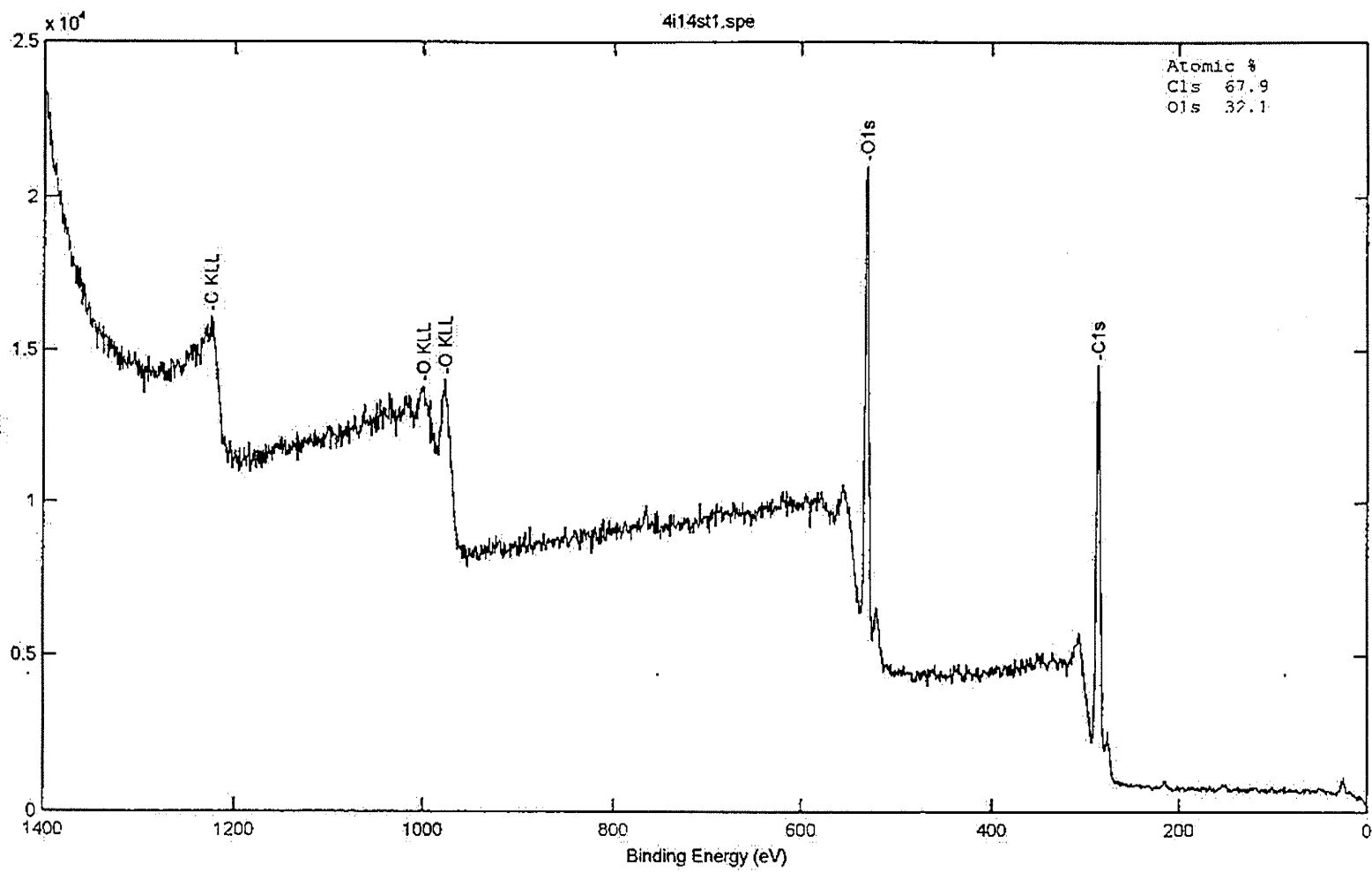


Figure L.1.(a) ESCA curves for COT-1

4i14st2.spe: ech. M. King: cotton-control, 2
04 Oct 14 Al std. 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

UBB/CRSFA
2.3405e+004 max
6.42 min

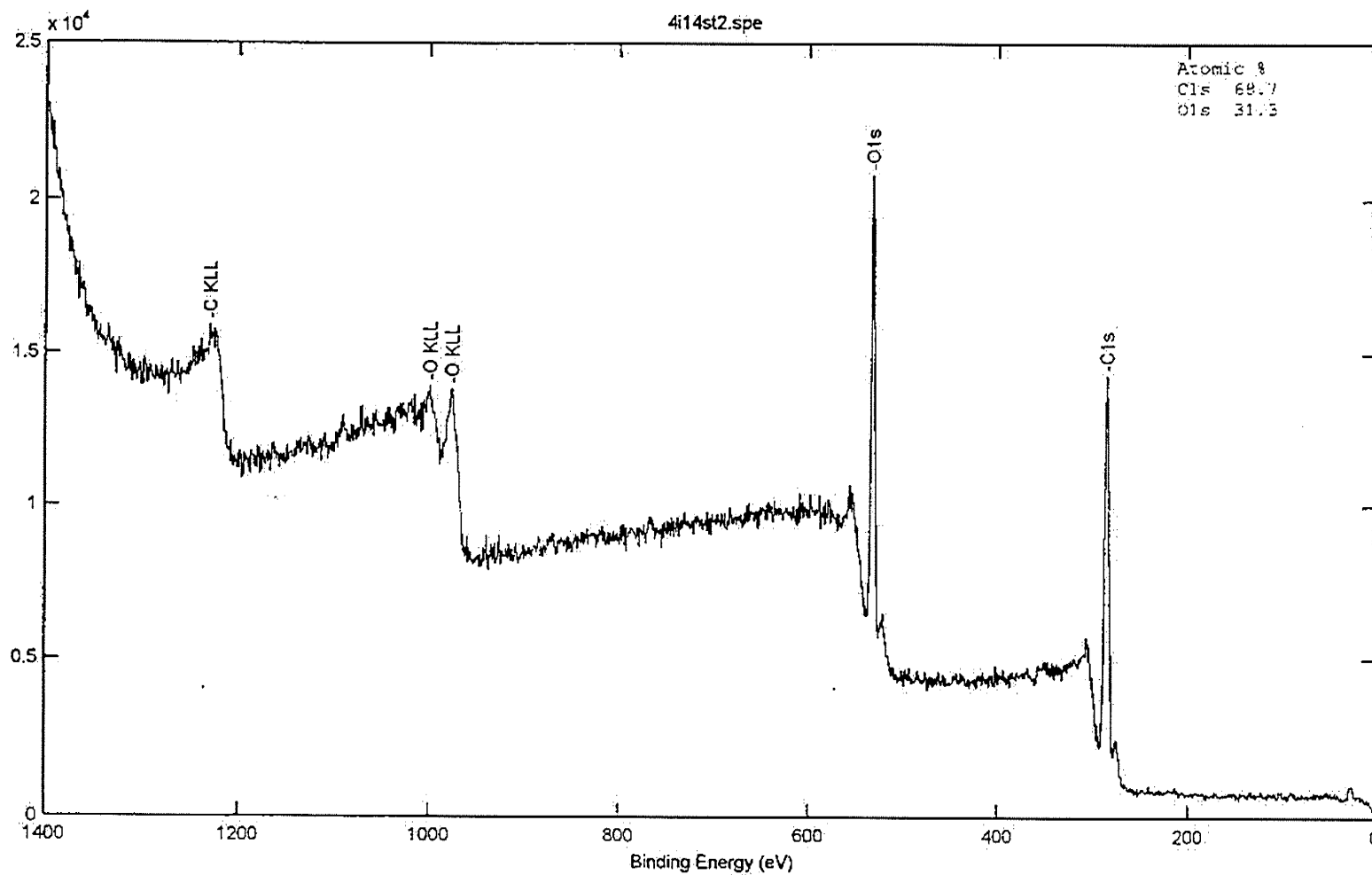


Figure L.1.(b) ESCA curves for COT-2

Figure L.1.(c) ESCA curves for COT-3

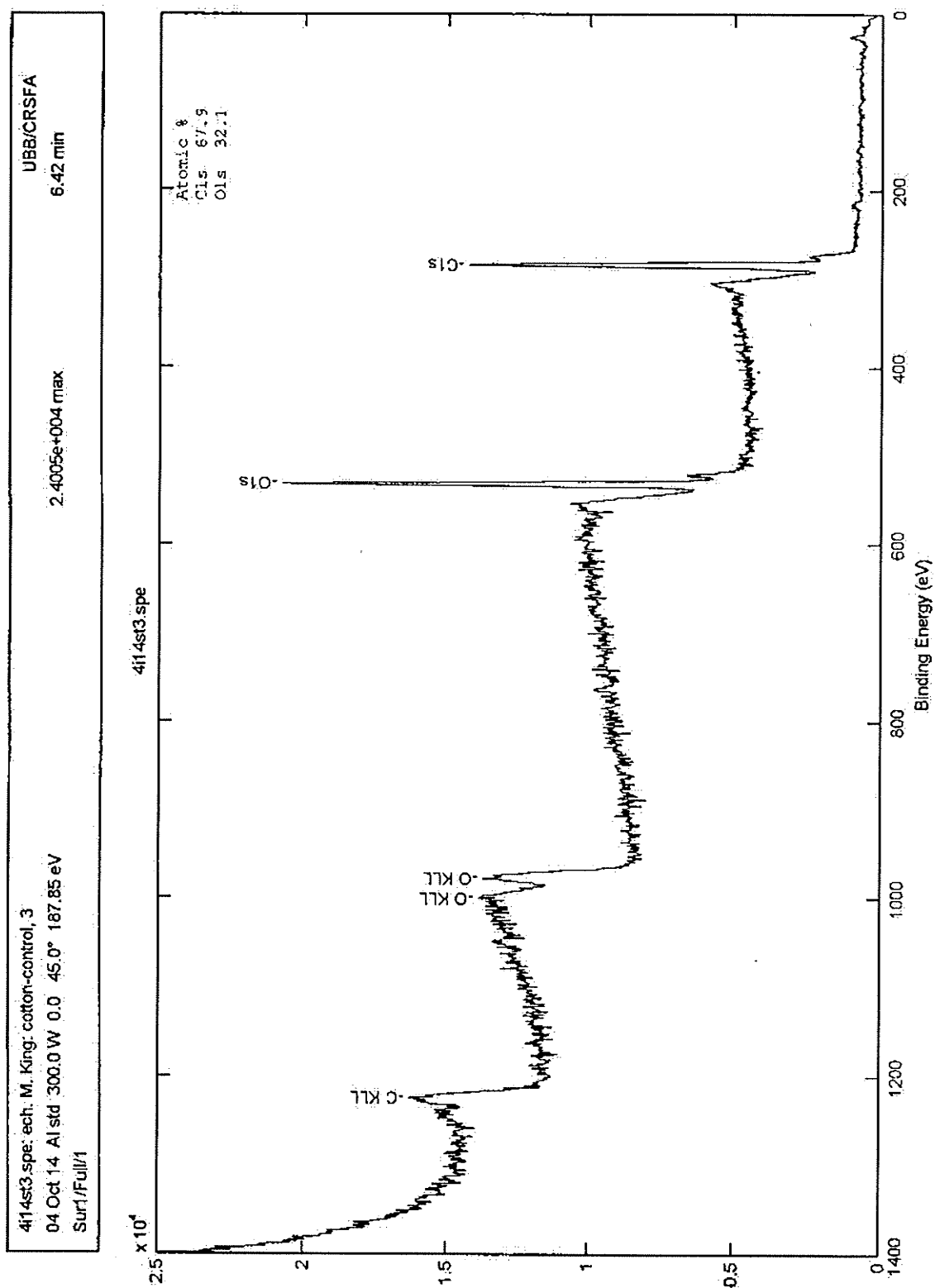


Figure L.2.(a) ESCA curves for CO2 -1

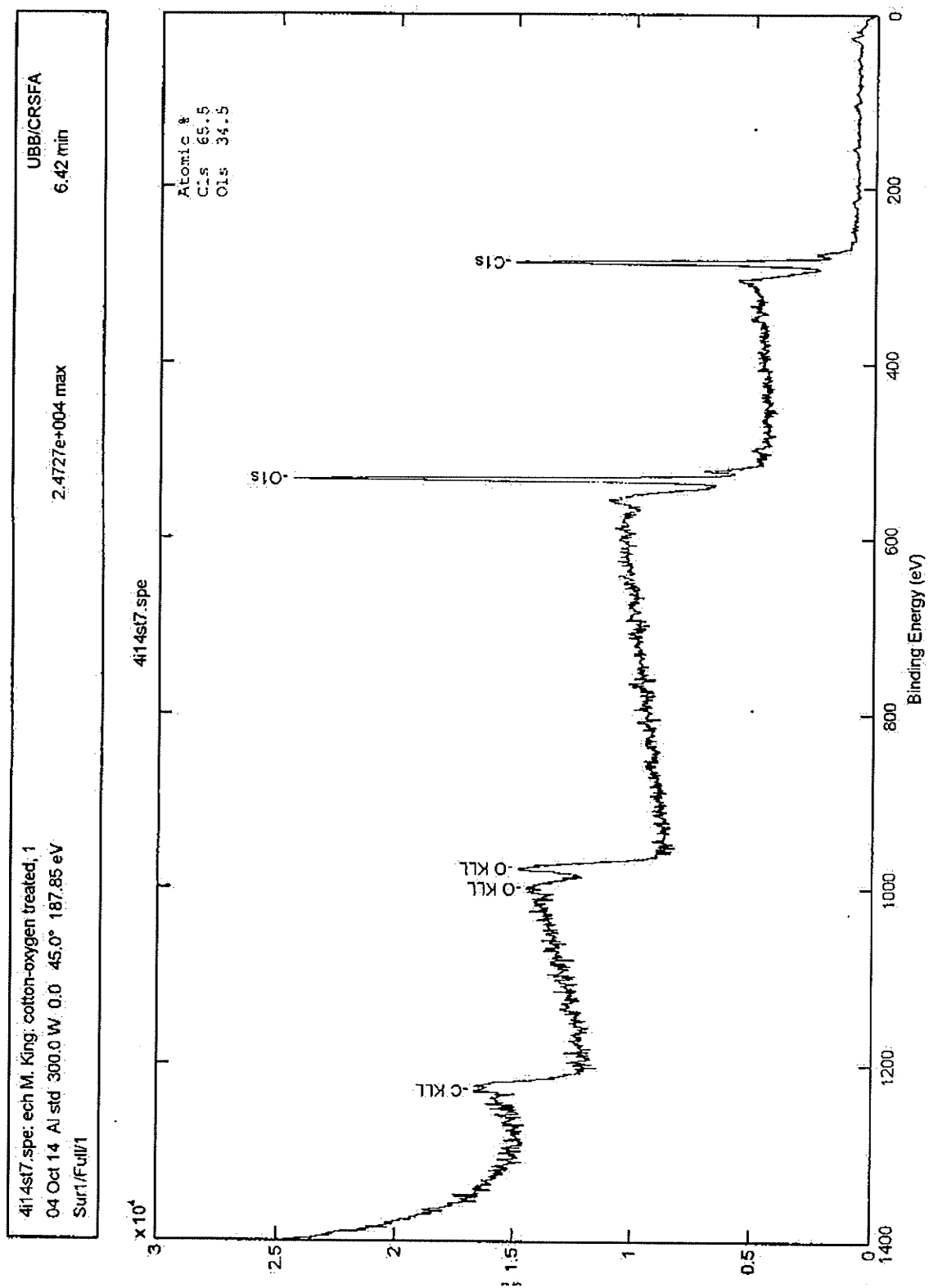
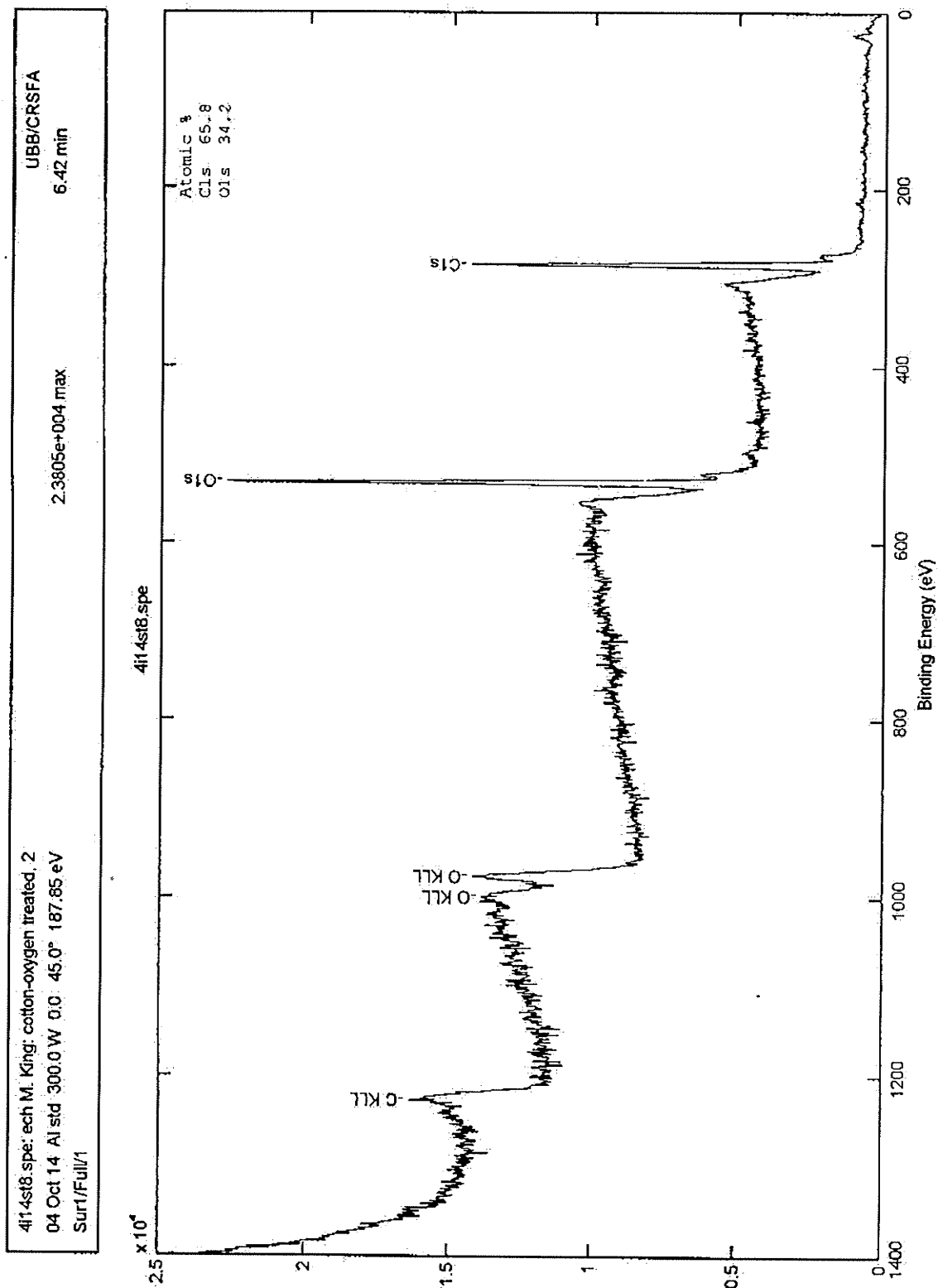


Figure L.2.(b) ESCA curves for CO2 -2



4i14st9.spe: ech M. King: cotton-oxygen treated, 3
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.3895e+004 max

UBB/CRSFA
6.42 min

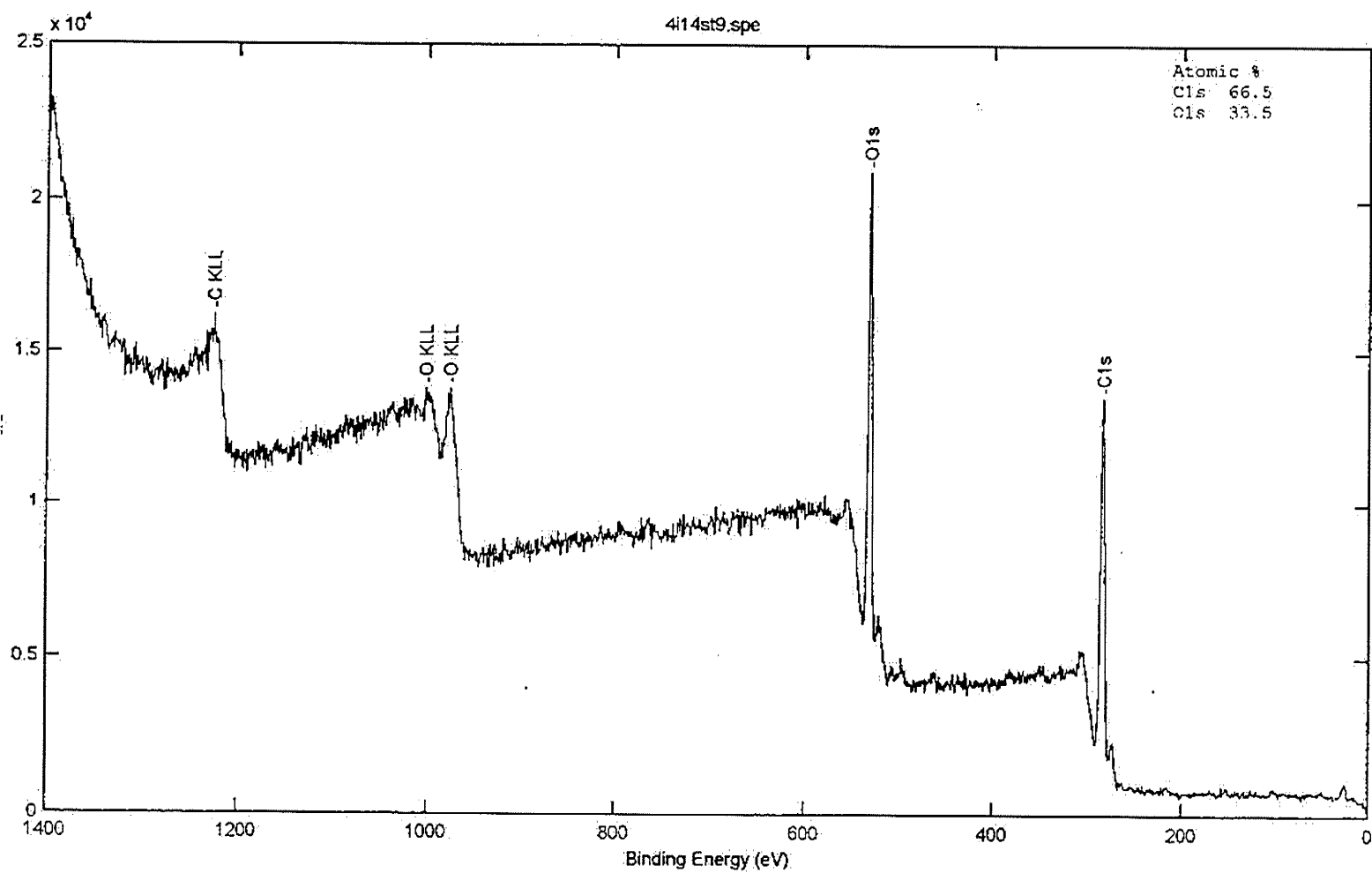


Figure L.2.(c) ESCA curves for CO2-3

4i14st4.spe: ech M. King: cotton-fluorine treated, 1
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.4850e+004 max

UBB/CRSFA
6.42 min

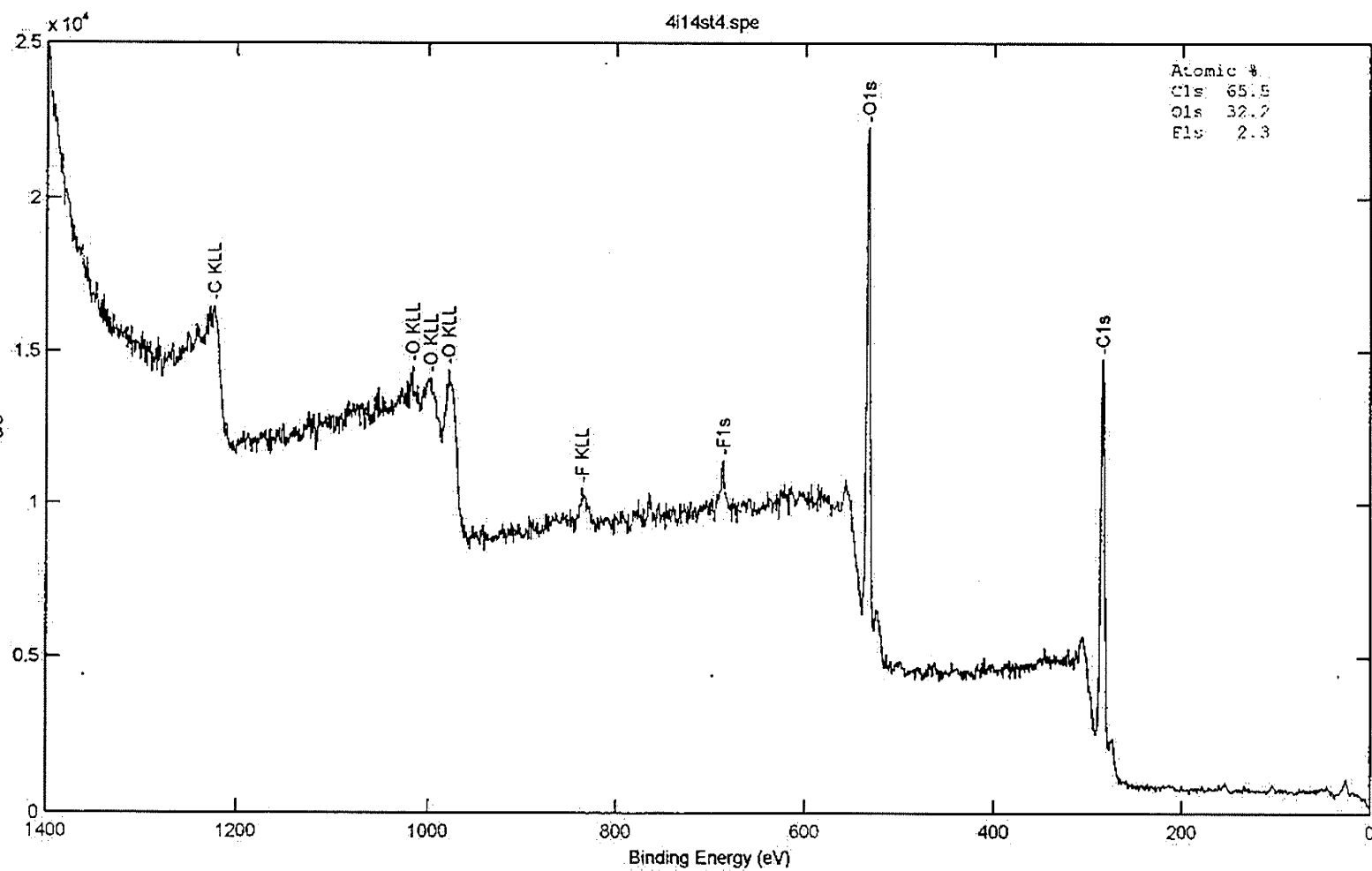


Figure L.3.(a) ESCA curves for C_F-I

4i14st5.spe: ech M. King: cotton-fluorine treated, 2
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.3800e+004 max

UBB/CRSFA
6.42 min

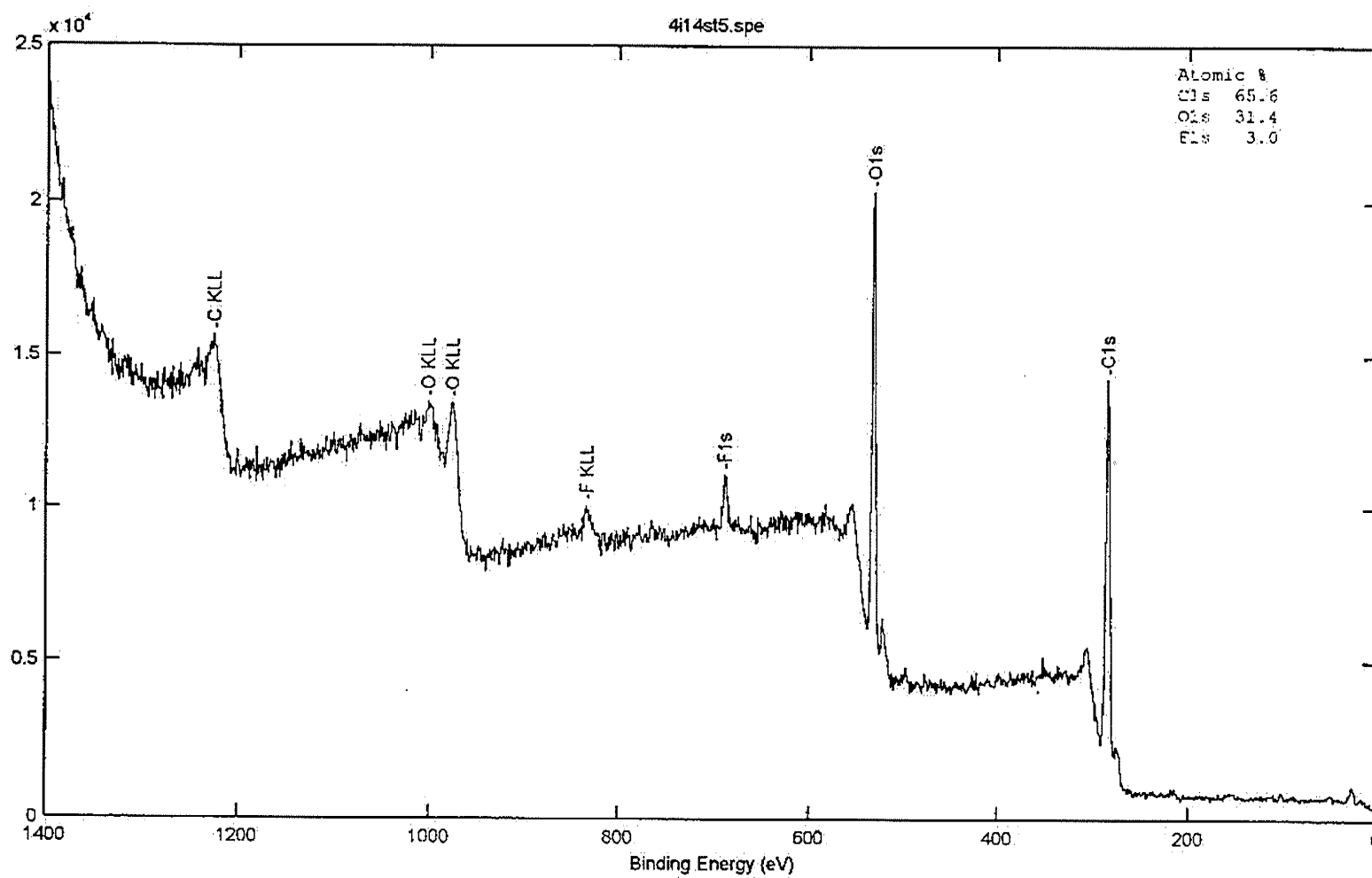


Figure L.3.(b) ESCA curves for C_F-2

4i14st6.spe: ech M. King: cotton-fluorine treated, 3
04 Oct 14, Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.3268e+004 max

UBB/CRSFA
6.42 min

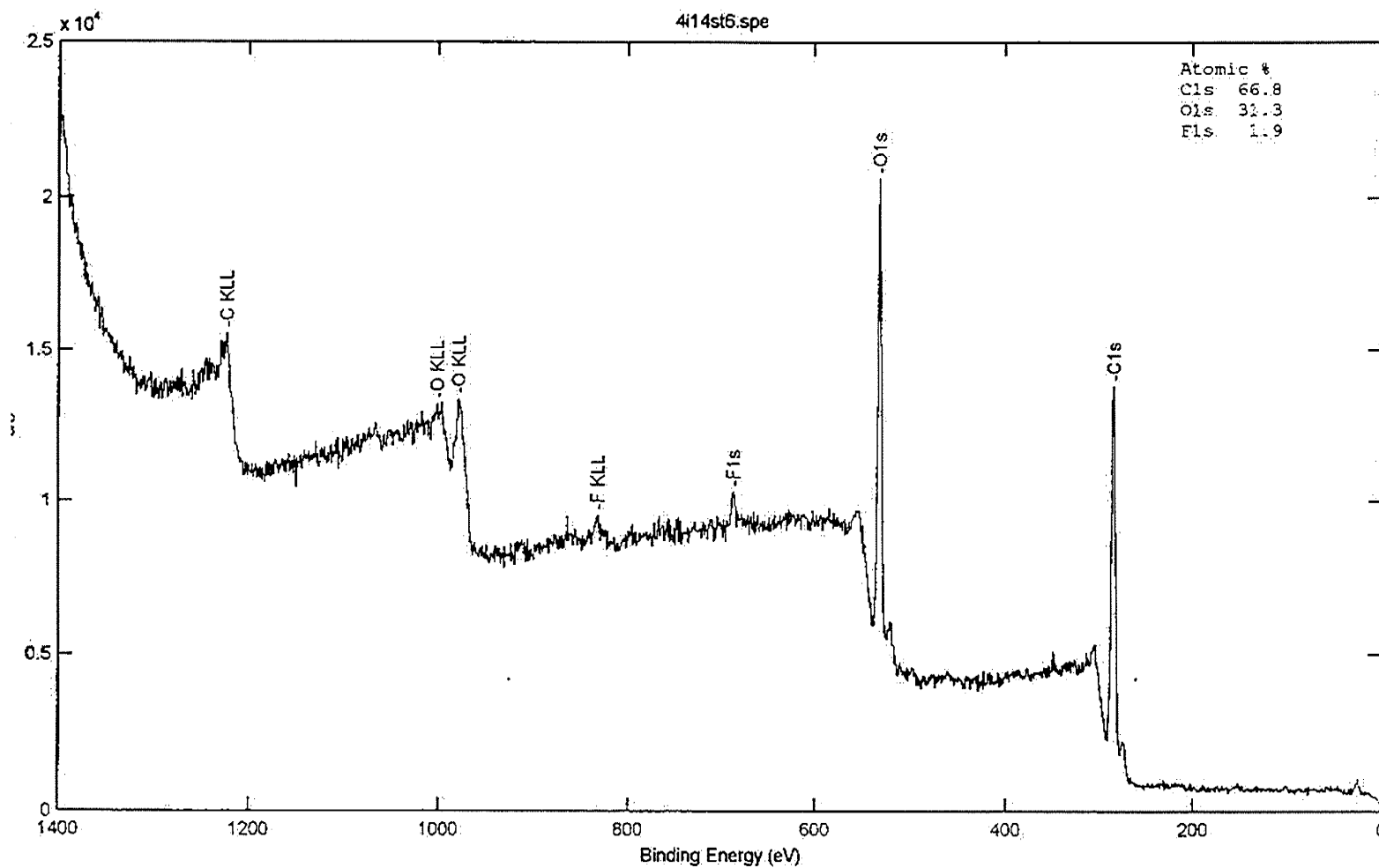


Figure L.3.(c) ESCA curves for C_F-3

4i14st10.spe: ech M. King: polypro-control_1
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

4.7045e+003 max

UBB/CRSFA
6.42 min

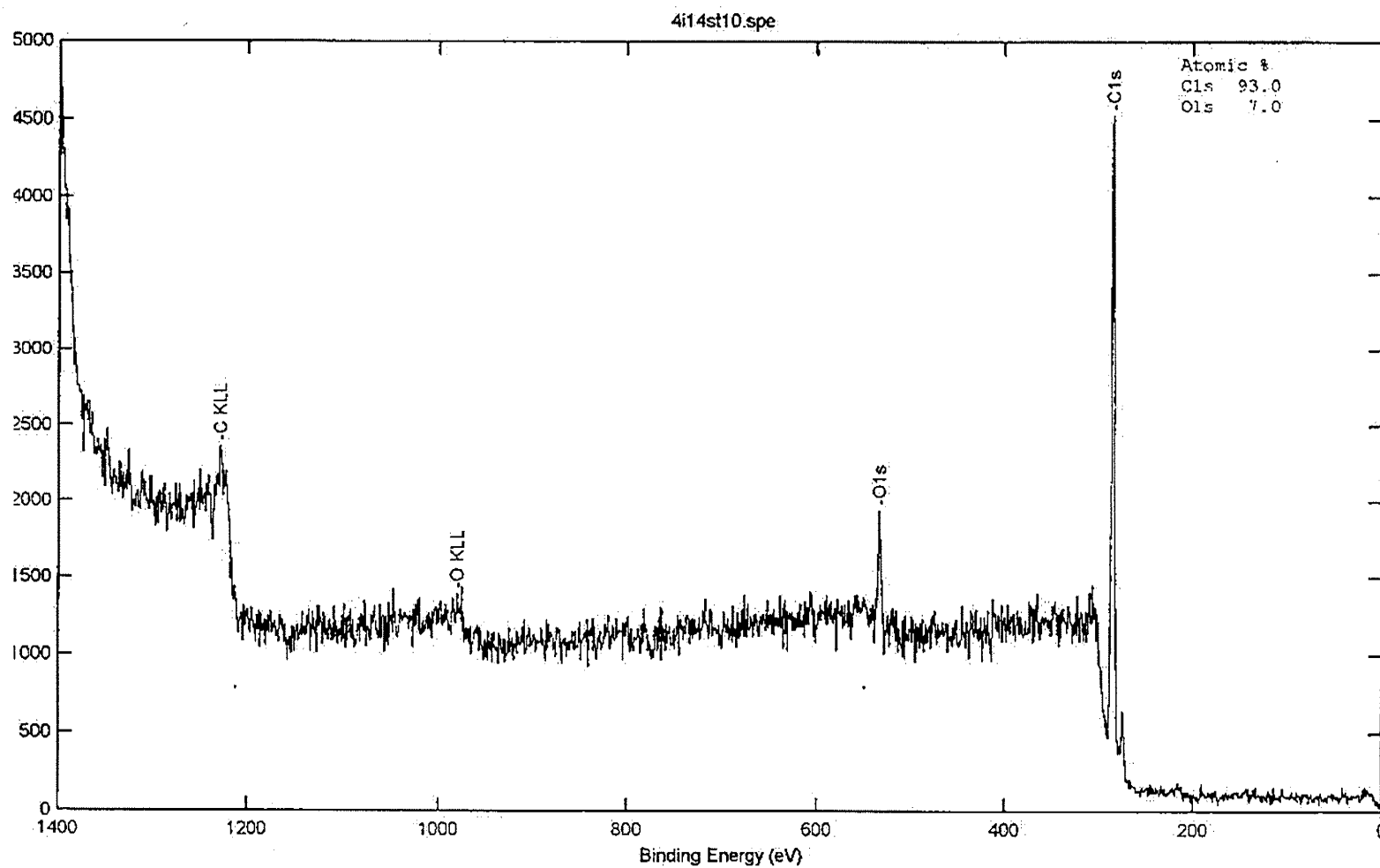


Figure L.4.(a) ESCA curves for PLV-1

4i14st11.spe: ech M. King: polypro-control, 2
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.5991e+004 max

UB6/CRSFA
6.42 min

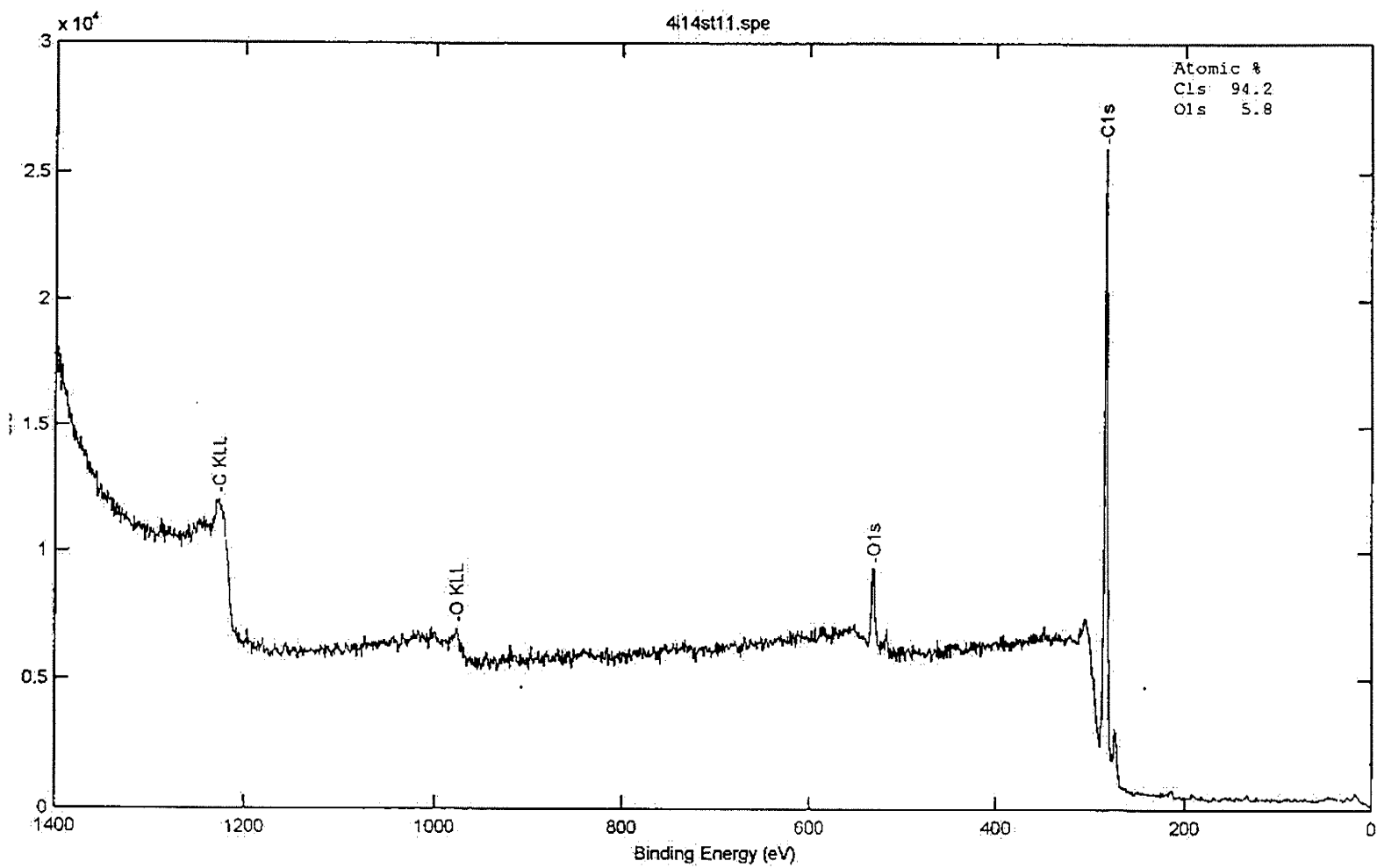


Figure L.4.(b) ESCA curves for PLY-2

4i14st12.spe: ech M. King: polypro-control, 3
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.5786e+004 max

UBB/CRSFA
6.42 min

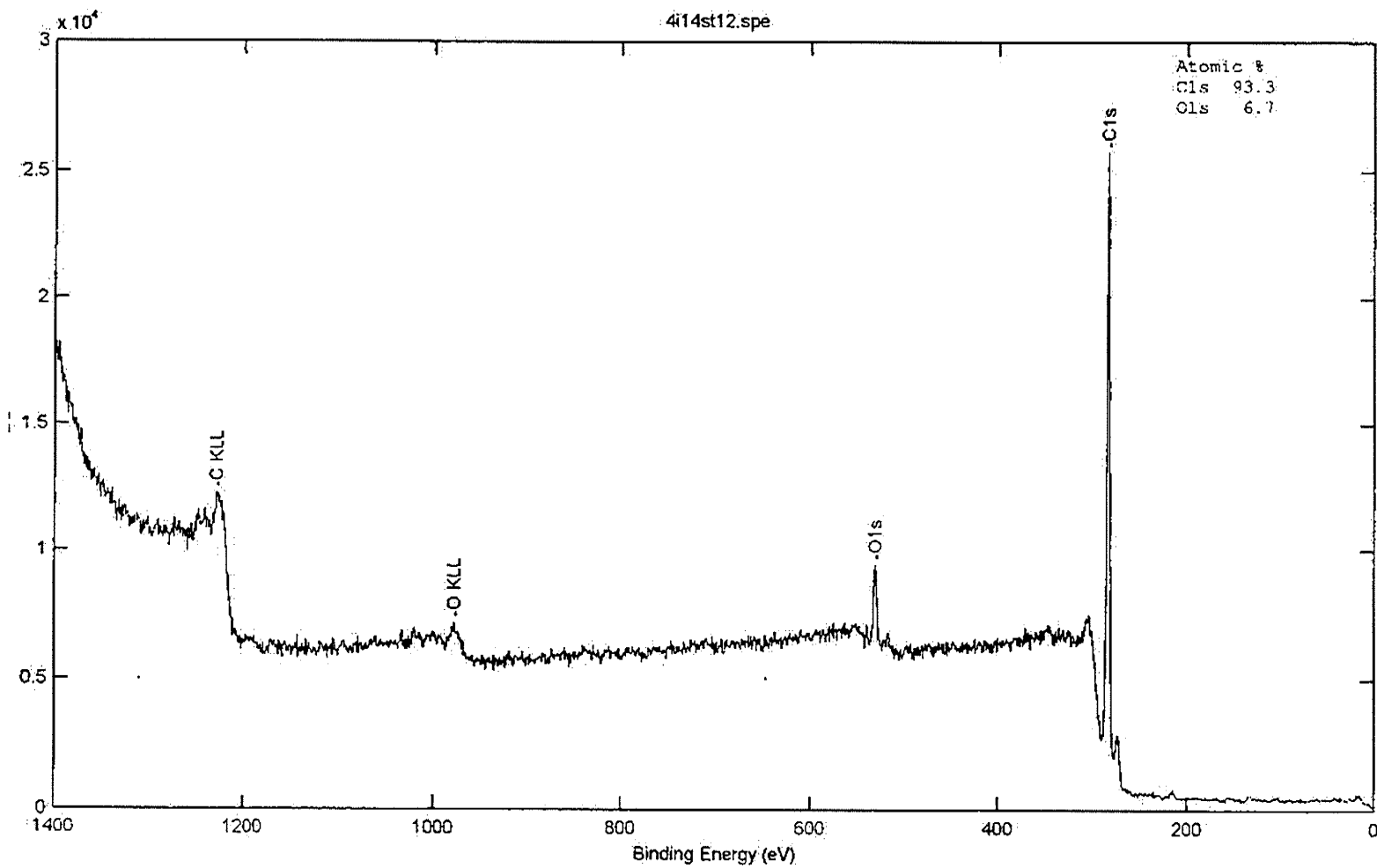


Figure L.4.(c) ESCA curves for PLV-3

4i14st16.spe: ech M. King: polypro-oxygen treated, 1
 04 Oct 14: Al std 300.0 W 0.0 45.0° 187.85 eV
 Sur1/Full/1

2.3895e+004 max

UBB/CRSFA
 6.42 min

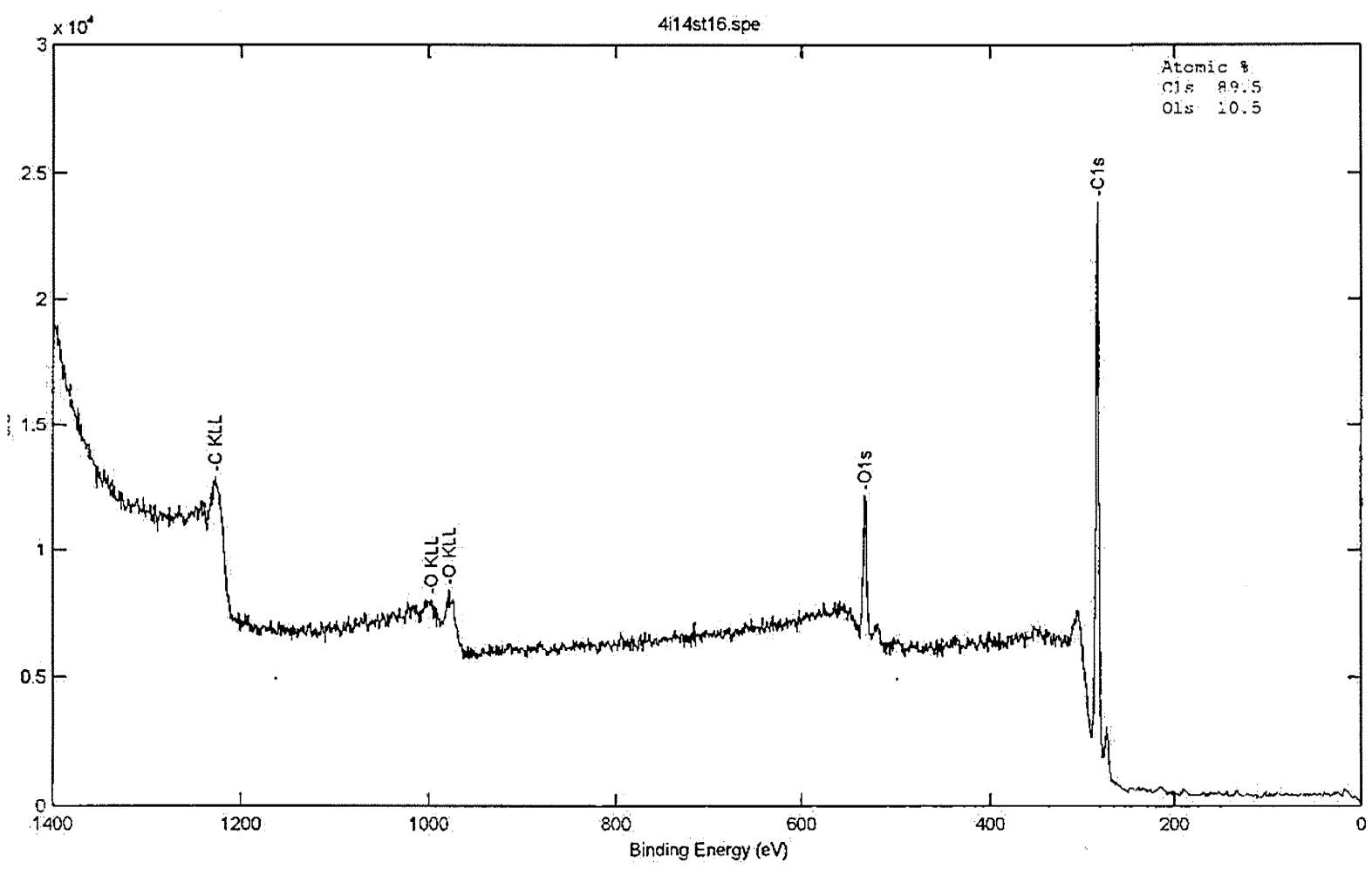


Figure L.5.(a) CA curves for PO2-1

Figure L.5.(b) ESCA curves for PO2-2

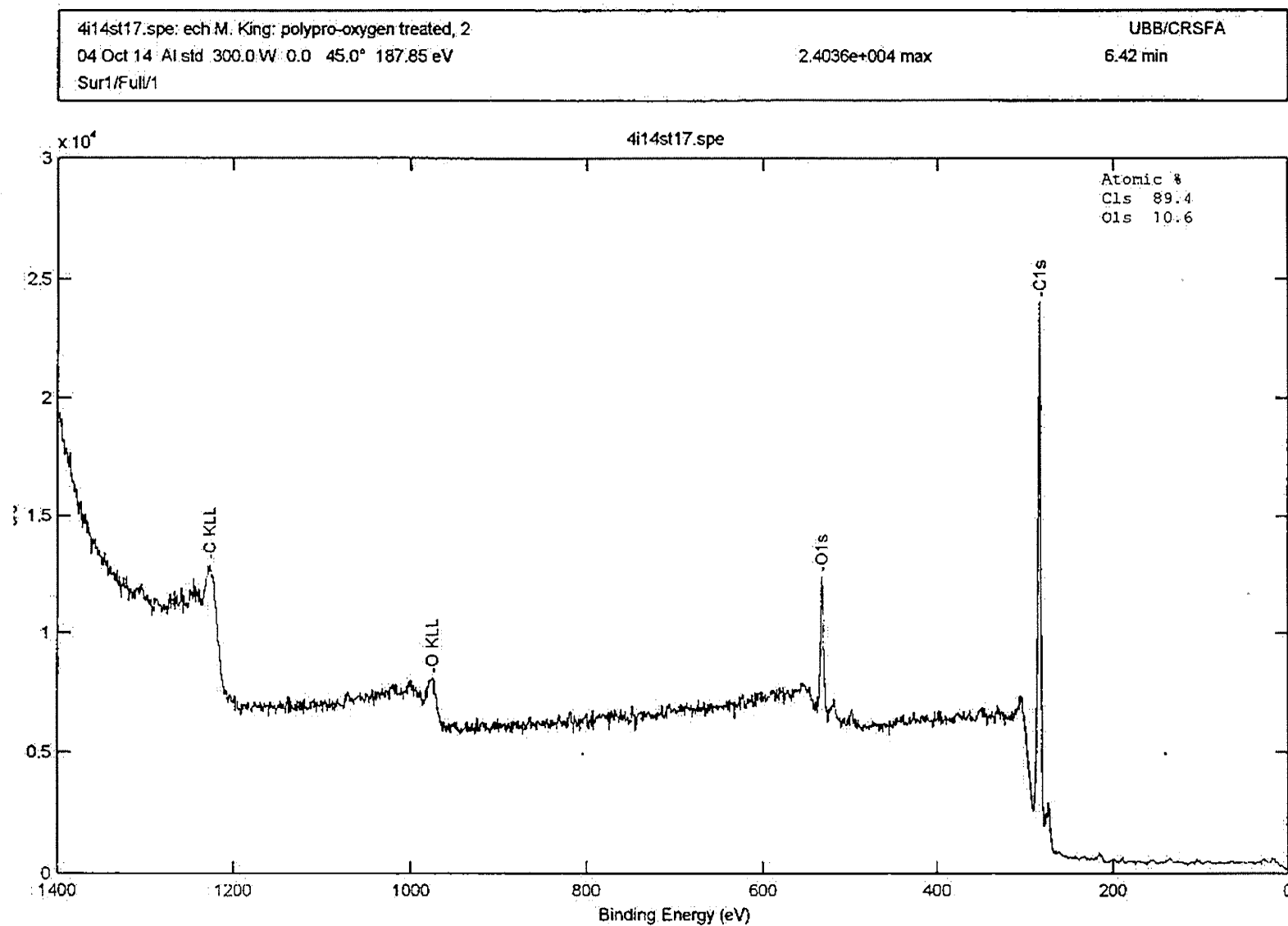
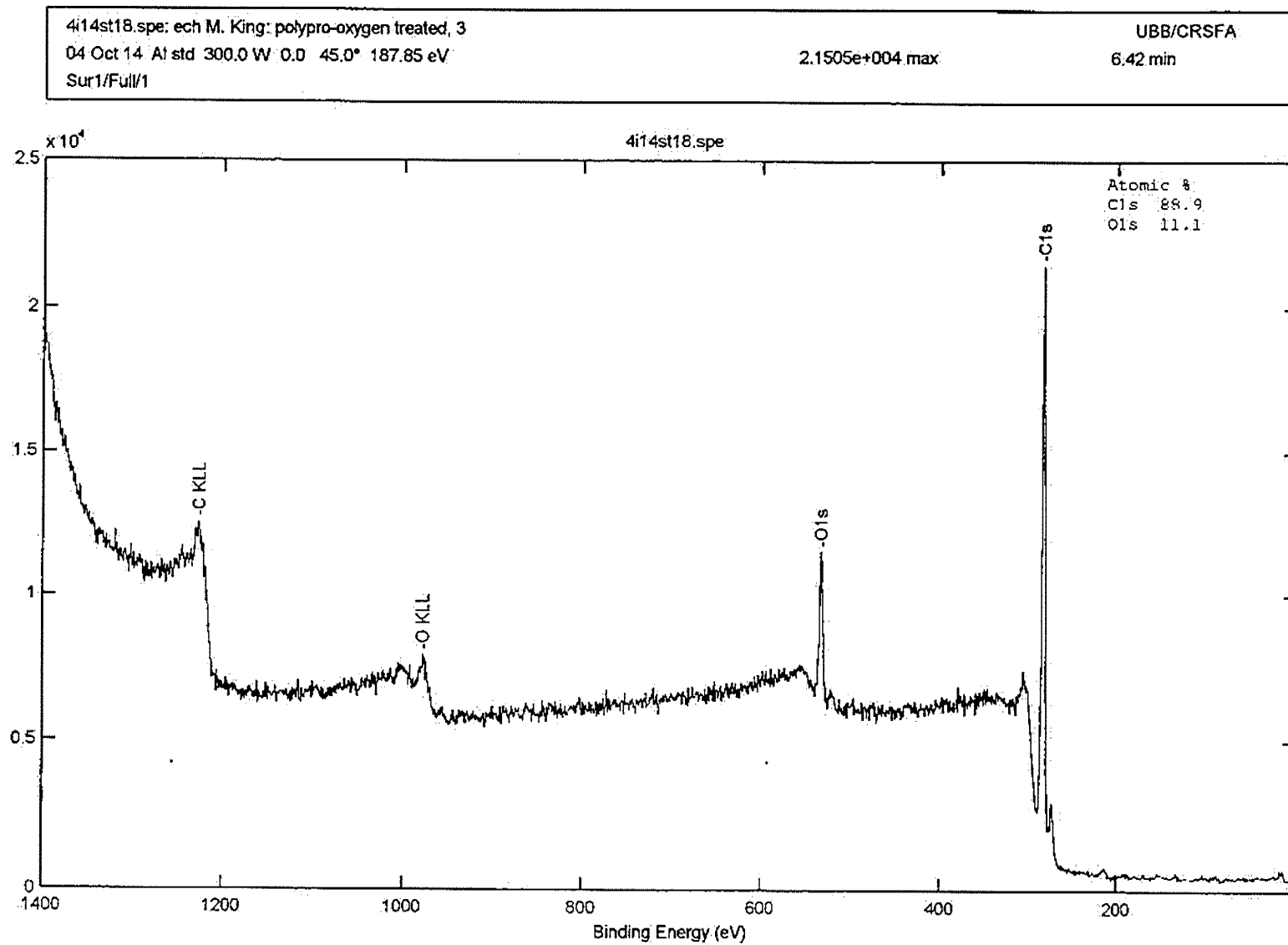


Figure L.5.(c) ESCA curves for PO2-3



4i14st13.spe: ech M. King: polypro-fluorine treated, 1
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.2327e+004 max

U8B/CRSFA
6.42 min

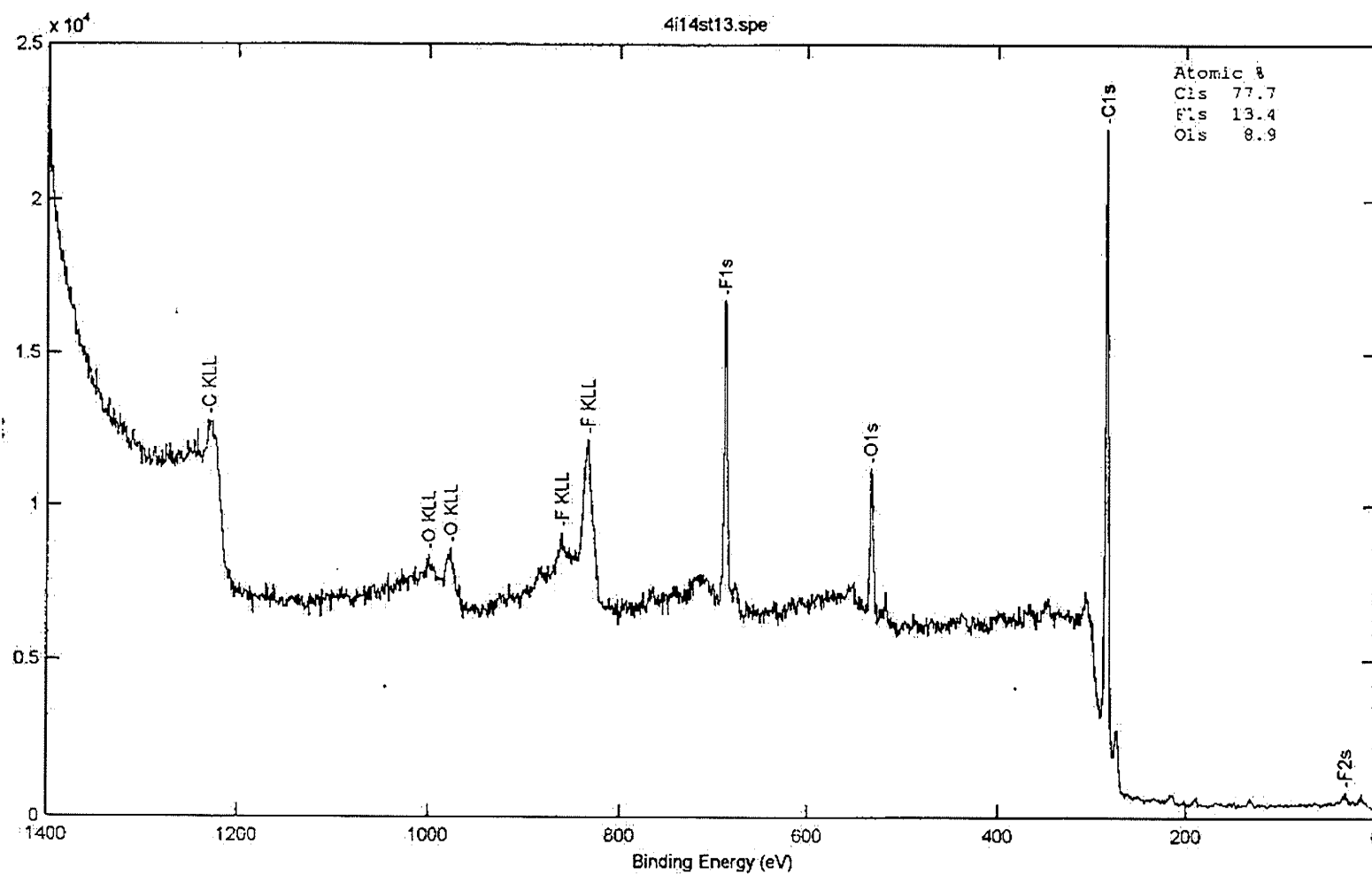


Figure L.6.(a) ESCA curves for P_F-1

4i14st14.spe: ech M. King: polypro-fluorine treated, 2
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full/1

2.4982e+004 max

UBB/CRSFA
6.42 min

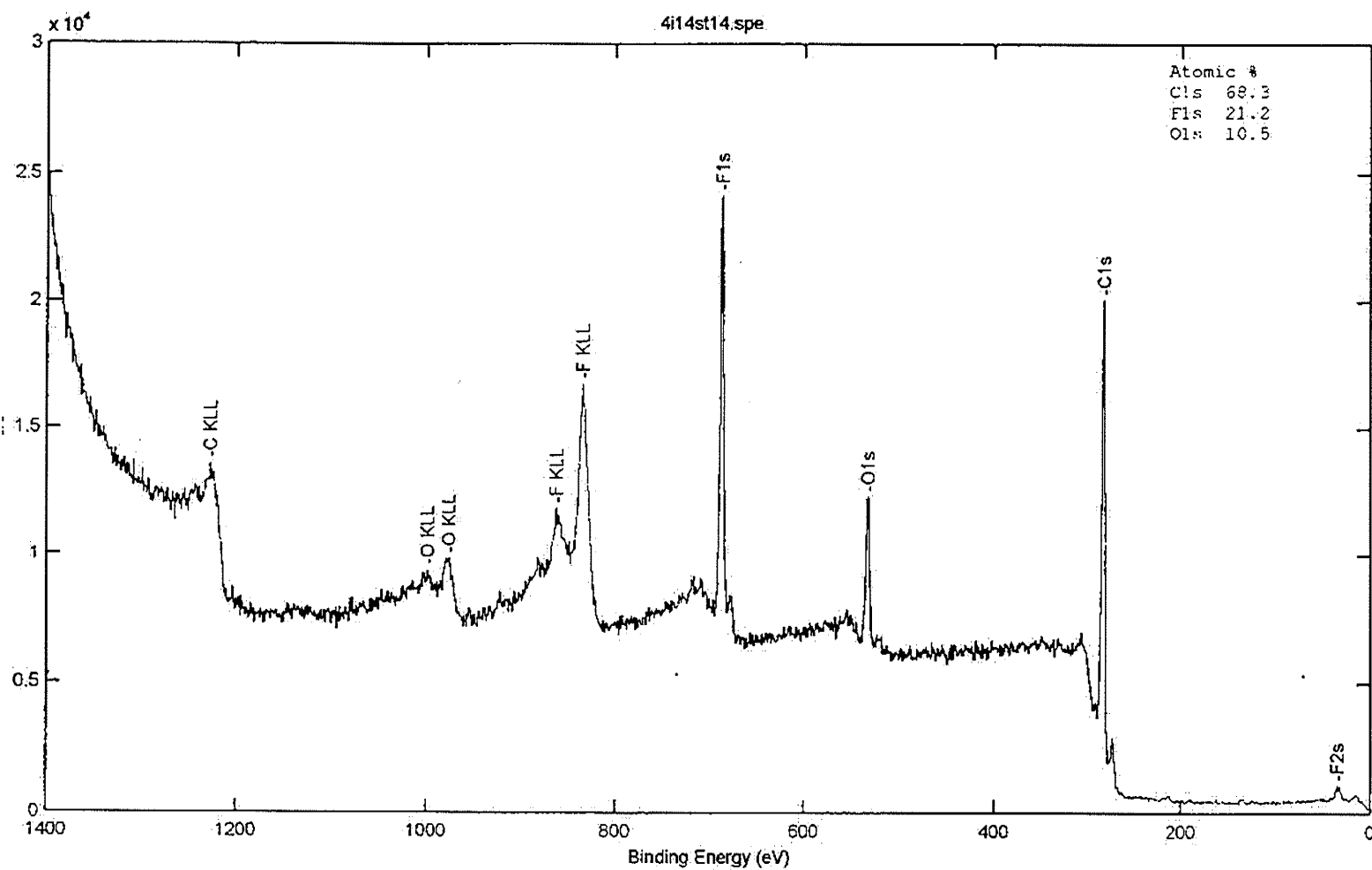


Figure L.6.(b) ESCA curves for P_F-2

4i14st15.spe: ech M. King: polypro-fluorine treated, 3
04 Oct 14 Al std 300.0 W 0.0 45.0° 187.85 eV
Sur1/Full1

2.1682e+004 max

UBB/CRSFA
6.42 min

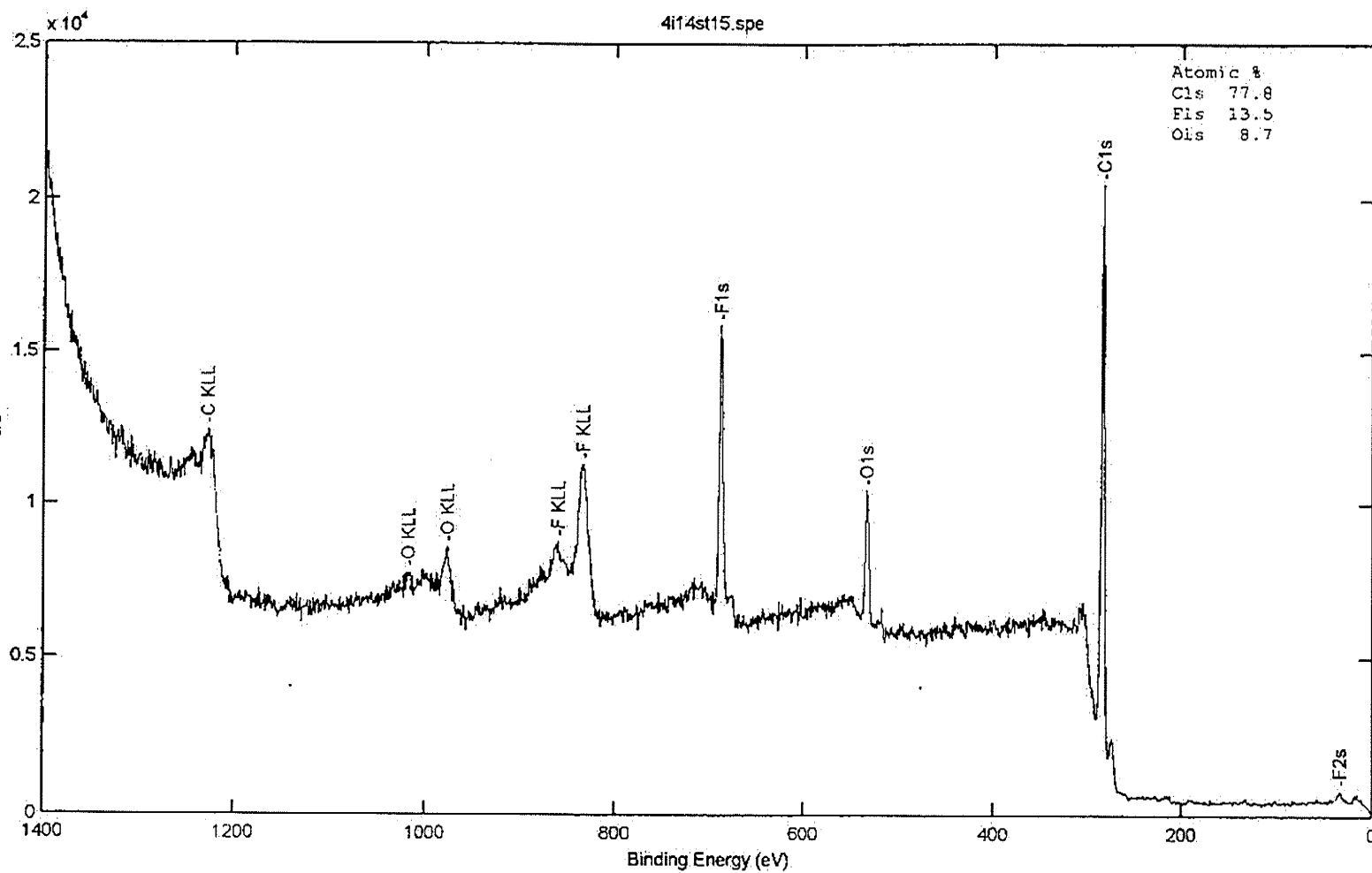


Figure L.6.(c) ESCA curves for P_F-3