# Discrimination of Retained Solvent Levels in Printed Food-Packaging Using Electronic Nose Systems

**David Van Deventer**

Thesis submitted to the faculty of
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

**Master of Science**
in
**Biological Systems Engineering**

Parameswarakumar Mallikarjunan, Chair
John Cundiff
Gene Haugh
Joseph Marcy

September 4th, 2001
Blacksburg, Virginia

Keywords: Electronic Nose, Response Surface Methodology, Retained Printing Solvents

# Discrimination of Retained Solvent Levels in Printed Food-Packaging Using Electronic Nose Systems

David Van Deventer

## (ABSTRACT)

The expanding role of electronic nose instrumentation, as a quality-monitoring tool for food-packaging materials, is examined and reviewed. The food industry is interested in determining the applicability of using an electronic nose for odor analysis of retained printing solvent levels in packaging. Three electronic nose systems were optimized for this application and their performance assessed. These include the FOX 3000, the Cyranose 320, and the QMB6.

Response surface methodology was used to generate $2^{nd}$ order models of sensor response as a function of system and experimental parameters for the three electronic nose systems. Forty-seven of 50 sensor models generated were found to be significant at an $\alpha$-level of 0.05. Optimum settings, that allowed adequate signals to be obtained for the full range of examined retained solvents levels, were selected for the remaining work using these models.

Performance analyses of these systems, which use three leading sensor technologies, showed that the conducting polymer sensor technology demonstrated the most discriminatory power. All three technologies proved able to discriminate among different levels of retained solvents. Each complete electronic nose system was also able to discriminate between assorted packaging having either conforming or non-conforming levels of retained solvents. Each system correctly identified 100% of unknown samples. Sensor technology had a greater effect on performance than the number of sensors used. Based on discriminatory power and practical features, the FOX 3000 and the Cyranose 320 were superior. The results indicate that electronic nose instrumentation can be used as a complimentary discriminatory tool in quality control.

## Table of Contents


| Title | Page |
|---|---|
| **Chapter 1 – Introduction** | 1 |
| Project Objectives | 4 |
| **Chapter 2 – Literature Review – Journal Review Paper** | 5 |
| **Chapter 3 – Journal of Food Science Paper: Electronic Nose Parameter Optimization** | 41 |
| Introduction | 42 |
| Materials and Methods | 43 |
| Results and Discussion | 47 |
| **Chapter 4 – Journal of Food Science Paper: Performance Analysis of Electronic Nose Systems in Discriminating Retained Solvent Levels in Packaging** | 78 |
| Introduction | 79 |
| Materials and Methods | 80 |
| Results and Discussion | 113 |
| **Recommendations** | 125 |
| **Vita** | 126 |

# Chapter 1

## Introduction

Packaging is an integral part of food processing. It has two major functions in the food industry: to protect the shelf life and quality of the food products, and to advertise the product at the point of sale. Factors that contribute to the deterioration of food products during transportation, distribution, and storage include mechanical forces such as impact and vibration, and environmental factors such as UV light, moisture, oxygen, and temperature. These factors can cause chemical or physical changes to the product, microbial contamination, pilferage or tampering of the product, and the migration of toxic compounds from the packaging material to the food (Sharma and others 2000).

Packaging material functions as a barrier between the product and the environment. It controls light transmission, and the transfer of heat, moisture, and gases. Changes in product quality and flavor due to aroma absorption and the transfer of undesirable volatiles from packaging to foods are important deterioration mechanisms when foods are packaged with polymer-based materials. This transfer of volatiles may lead to off-odor and off-taste development (Hotchkiss 1997). Thus, the migration of compounds, from the packaging to the product, is a major concern from both toxicological and sensory standpoints. Sources of compounds that may migrate into food from plastic films include ink solvents, adhesive systems used in laminations, and polymerization reactions in which a solvent is used as a reaction medium. Product packaging should function to retain desirable odors and prevent odor absorption from plasticizers, printing inks, adhesives, or solvents used in the packaging materials (Sharma and others 2000).

Diffusion is the primary mechanism for the transfer and migration of chemical compounds from the packaging materials to the food product. Concentration potential and free volume theory, which asserts that the molecular motion in the bulk state occurs due to the presence of holes or vacancies, are the most prevalent theories explaining the diffusion of molecules through solid materials (Ozdemir and others 1999). Additives used in the production of plastics to enhance their physical properties tend to migrate from the plastics due to their high mobility and low molecular weights. Possible migrants from plastics could be monomers, oligomers, plasticizers, antioxidants, antistatic and antifogging agents, colorants, emulsifiers and degradation products. Some plasticizers, which function to add softness and pliability to the

plastic, are of particular concern. These include phthalates and adipates. Migrating solvents such as abietic acid, toluene, butanone-2, ethyl acetate, and hexane are also of concern as well as pigments such as molybdate orange (Gilbert and others 1988; Ozdemir and others 1999).

In a study performed in 1989 by Castle and others, it was demonstrated that on polypropylene packaging, transfer of components from the ink on the outer surface of the film to the inner food contact surface occurred amounting to 6% of the total amount of plasticizers used in the printing system for dicyclohexyl phthalate. Plasticizers are widely used in plastic films and coatings, and are also used in printing inks. The plasticizers used in the ink printed on the outer surface of the packaging material are usually used at levels from 2% to 8%. They form an essential part of the printing ink formulation and contribute to the adhesion of the ink to the package. Plasticizers that are frequently used in such a manner include dibutyl, dicyclohexyl, and di(2-ethylhexyl) phthalate esters. In the same study, it was found that for all retail food samples tested, blank foods had negligible plasticizers levels and the packaged foods had plasticizers levels corresponding to those found in the packaging material (Castle and others 1989). The results of a study conducted by Nerin and others in 1993 support these findings and also found new plasticizers such as N-ethyl-toluene-sulphonamide. This particular plasticizer is often used as a substitute for phthalate plasticizers in printing inks. The plastics examined in these studies were oriented polypropylene that does not require the use of plasticizers to achieve the desired plasticity. Consequently, the migrating plasticizers that were studied came only from the printing inks used on the films (Nerin and others 1993).

In the food industry, the volatiles from plastic packaging films and their printing inks are analyzed using gas chromatography, gas chromatography-olfactory, and gas chromatography – mass spectroscopy. While these methods are useful research tools, they require extensive time and preparatory measures, and expertise in understanding the results. In addition, it is difficult to correlate results from human sensory analysis of complex aromas to the use of analytical techniques to identify individual components in a complex aroma. Currently, sensory panels are relegated to inspect a product before and after processing and analytical measures are used for monitoring during the production process. As a complimentary measure, the use of a chemosensory system or "electronic nose," has been introduced as a means to classify and characterize films and has the potential to be a useful tool in quality control.

Electronic noses are gas multi-sensor arrays that are able to measure aroma compounds in a manner that is closer to sensory analysis than gas chromatography. The system is composed of several sensors that may be set to achieve various levels of sensitivity and selectivity. The adsorption of volatiles on the sensor surface causes a physical change of the sensor, and a specific reading to be obtained for that sample. However, problems exist with the use of these sensors such as sensor drift and poor repeatability and reproducibility due to system sensitivity to changes in operational conditions or poor gas selectivity and sensitivity (Roussel and others 1998). In order to overcome these difficulties, it is necessary to develop a successful and efficient testing methodology at optimum parameter settings. Roussel and others in 1999 examined the influence of various experimental parameters on the multi-sensor array measurements using an electronic nose with $SnO_2$ sensors and attempted to quantify them. Volatile concentration in the headspace increased as the sample temperature is increased. In screening factorial experimental designs, it is necessary that the response of the experimental parameters be monotonic within a studied range. Alternatively, response surface designs must be generated in order to develop a model of the multi-sensor response.

There are currently three major technologies upon which commercial electronic nose systems have been developed; metal oxide semiconductors, semiconducting polymers, and quartz crystal microbalance sensors. A select number of companies also produce systems using metal oxide semiconductor field effect transistors technology. The determination of which of the three aforementioned types of electronic nose systems, if any, that would be most suitable as a discriminatory analysis tool to be used in quality control is of interest in the food industry.

**Significance and Rationale**

The food industry is interested in additional methods of quality control to discriminate between ‘conforming’ and ‘non-conforming’ packaging films based upon the levels of volatiles in printing inks and organic solvents that affect flavor characteristics as well as the wholesomeness of the food product. The use of electronic nose sensor technology to determine characteristic recognition patterns or ‘fingerprints’ of packaging containing conforming and non-conforming retained solvent levels has shown potential as a discriminatory analysis tool. It has the potential to compliment sensory analysis and augment the gas chromatography analysis measures currently used in the food industry because it requires less extensive operating and preparatory measures, less expertise to interpret the results, and analyzes complex aromas.

Subsequently, the determination of which of the three types of electronic nose technologies, if any, that would be most suitable as a discriminatory analysis tool to be used in quality control is of interest in the food industry.

**Hypothesis**

Electronic nose systems using different technologies can perform effectively in discriminating between plastic food packaging films with conforming and non-conforming volatile levels with the most effective system being the electronic nose system based upon the quartz-microbalance technology.

**Objectives:** The following research objectives are addressed for each of the electronic nose systems; Alpha M.O.S. FOX 3000, Cyrano Sciences Cyranose 320, and HKR Sensorsystems QMB6:

1. To optimize the electronic nose for adequate detection levels of volatiles from the packaging films in the sample headspaces.
2. To develop databases of recognition patterns for various film samples that are known to have conforming retained solvent levels and non-conforming retained solvent levels as designated by the supplying manufacturer.
3. To test the ability of the electronic nose to accurately classify unknown samples as having either conforming or non-conforming retained solvent odor levels.
4. To comparatively assess the electronic nose systems based upon their ability to discriminate between samples in the application of quality monitoring of retained printing compounds in food-packaging.

## Chapter 2 – Literature Review

## Electronic Nose Applications In Analyzing Printing Solvent Off-Odors in Plastic Food-Packaging: A Review

**Summary**

Electronic nose instrumentation is comprised of gas multi-sensor arrays that are able to measure aroma compounds in a manner that is closer to sensory analysis than gas chromatography. This feature indicates a potential for electronic nose chemosensory systems to be used as a complimentary tool in the monitoring of odors from printing inks and solvents used on plastic food-packaging films. The expanding role of electronic nose instrumentation as an additional quality-monitoring tool in this application is reviewed.

**Keywords:** food packaging, electronic nose, chemosensory systems, retained solvents

### Introduction

Phthalate esters, particularly di-2-ethylhexyl phthalate (DEHP), were used heavily in the past as plasticizers in polymer films used for food packaging. When it was revealed to be a health threat and a proven carcinogen in animals, its use in polymer films for the food industry was discontinued. However, it is still used in minor amounts as a plasticizer in the printing inks used on these films. Consequently, it may still pose a health threat if it were to migrate through the packaging films and into the food product. Printing solvents used also pose quality concerns as a source of off-odors if they are retained at high levels.

A major role of packaging is to maintain product quality until user consumption. Package-product interactions may degrade product quality if important flavor compounds are scalped from the product by the package or if compounds migrate from the package and interact with the food product. Currently, human sensory panels and gas chromatography techniques are used to monitor odors from the printing process that pose a threat to product quality.

Although these techniques provide useful information, there are numerous shortcomings. Electronic nose instrumentation may be developed in this application as a complimentary tool that could bridge many of the gaps. Electronic nose perception of aroma volatiles involves reversible reactions of those compounds in the aroma with an array of sensors, and then using statistical methods to compare the results to those of a known database. There are several different technologies upon which electronic nose instrumentation is based. An analysis of three of the most prominent technologies used commercially in this application of printing odors in

food packaging is of interest to the food industry. The facets involved in developing electronic nose instrumentation as a complimentary tool in this application are reviewed.

**Food Packaging**

Packaging is an integral part of the processing of food products. It has two major functions in the food industry: to protect the shelf life and quality of the food products, and to advertise the product at the point of sale. Factors that contribute to the deterioration of food products during transportation, distribution, and storage include mechanical forces such as impact and vibration, and environmental factors such as UV light, moisture, oxygen, and temperature. These factors can cause chemical or physical changes to the product, microbial contamination, pilferage or tampering of the product, and the migration of toxic compounds from the packaging material to the food (Sharma and others 2000).

Packaging material functions as a barrier between the product and the environment. It controls light transmission, and the transfer of heat, moisture, and gases. However, when the package and the product interact at an unacceptable level, adulteration of the product quality and a reduced shelf life may occur. Changes in product quality and flavor due to aroma absorption and the transfer of undesirable volatiles from packaging to foods are important mechanisms of deterioration when foods are packaged with polymer-based materials and may lead to off-odor and off-taste development (Hotchkiss 1997). Thus, the migration of compounds from the packaging to the product is a major concern from both toxicological and sensory standpoints. Product packaging should function to retain desirable odors and prevent odor absorption from plasticizers, printing inks, adhesives, or solvents used in the packaging materials (Sharma and others 2000).

Distinctions are usually made between levels of packaging. Of particular interest here are the primary printed packaging films used for snack foods and specific types secondary printed packaging films that are used, for example, as a tray over-wrap of individual primary packages. In both cases, there is a potential for compounds originating from the printing process to migrate and interact with the food product.

**Polymer Films**

Although there are many different polymers used to package snack foods and confectionaries in the food industry, the polymers of concern in this study include low-density polyethylene (LDPE), oriented-polypropylene (OPP), and polyethylene terephthalate (PET).

These polymers are treated with various processes and orientation to achieve desirable characteristics. Additives are often used to alter blocking, coefficient of friction, clarity, and pliability characteristics.

LDPE is the largest volume polymer used in the food industry in both the film and blow-molded form (Robertson 1993). LDPE is a polyolefin, which can develop a wax-like odor at high temperatures. It is a tough, translucent material with a $T_{melting}$ of 98 °C and $T_{glass\ transition}$ of –25 °C. Although LDPE packaging of snack foods is not generally exposed to high temperatures, another potential source of off-odors in LDPE comes from the use of fatty acid amide as a slip additive and long-term storage or oxidative conditions (Robertson 1993). LDPE is an excellent water vapor barrier, although it is highly permeable to gases. PET is a polyester with a $T_{melting}$ of 267 °C and $T_{glass\ transition}$ that is between 67 °C and 80 °C. The PET films that are widely used are generally biaxially oriented and used to add rigidity and support to multilayer standup pouches. OPP is a polyolefin with a $T_{glass\ transition}$ of –18 °C and a $T_{melting}$ of 176 °C. It is a linear compound. Oriented polypropylene has seen a large increase in use in the food industry in recent years and has a much greater tensile strength the cast polypropylene films. One important property of polypropylene is its high resistance to fatigue by flexing. Orientation of the polymer increases strength, tear resistance, and also increases resistance to water vapor permeation. The gas and odor barrier properties that are poor in OPP alone can be enhanced through lamination with another polymer or through the formation of metallized OPP through electrostatic deposition (Robertson 1993). Polypropylene, with a density of 0.9 g/cc, is the lightest resin used in food packaging. It also has greater clarity and is stiffer and tougher than polyethylene films (Jenkins and Harrington 1991). The recycling code number for OPP is 5, 4 for LDPE, and 7 for others including multilayer packaging films (Selke 1994).

Commercially produced snack foods are currently packaged with a variety of single or multi-layer polymer films. Types of films used include OPP, metallized-OPP, LDPE, and polyesters such as PET films for multi-layer packages. Reverse printed OPP – adhesive – HDPE – seal layer, is a primary structure in use in snack food packaging (Jenkins and Harrington 1991). Reverse printed OPP – adhesive or PE – metallized OPP – seal, or two coextruded OPP layers with a seal layer are other commonly used packaging structures. The particular structure used is based upon product needs regarding barrier properties, rigidity, nature of the seal, clarity and printing surface, and cost. Chocolate blocks are more commonly packaged in foils laminated

with LDPE that may be heat-sealed and is a better moisture and odor barrier than foil or foil-paper barriers. Another commonly used package in the snack food industry utilizes a metallized-OPP foil sealed with cold-seal adhesive.

**Health Threat**

Consumer concern regarding the wholesomeness and safety of food products has increased dramatically in the past century. Potential health threats associated with food packaging are due to product–package interactions and product adulteration or pilferage.

Product-package interactions also a pose a quality concern for the product before it reaches the end-consumer, as it is a source of off-odor and off-flavor generation or aroma scalping. The potential migration of compounds from any packaging into the product at concentrations significant to be harmful is a health threat. A variety of chemical reactions can occur during package-product interactions due to the complex structure and chemical composition of the packaging films. The reactions occur between packaging components themselves, or packaging and product components, with some compounds acting as catalysts. These reactions often form compounds with low odor thresholds that diffuse into the product or the package headspace (Robertson 1993).

The principle of the 'inertness' of the food packaging material and purity or wholesomeness of the food product as it reaches end-use has been a focus of regulating agencies in addressing this food threat. The issue of concern is the toxicity of additive chemicals at the concentrations found in the food product not the concentrations found in the packaging material. Compounds of particular concern involved with plastic food packaging include several plasticizers and organic solvents used in the plastic films themselves and in the inks, adhesives, and processing during printing (Chapter 20) (Robertson 1993).

**Inks, Plasticizers, and Solvents**

During the printing process of polymer film materials, the inks and adhesive formulations used are diluted or dissolved in organic solvents that are later removed through evaporation as the printed films are passed through dryers. Printing solvents that are retained on the packaging films after the drying process at significant residual levels could form off-odors that may migrate through the packaging and interact with the food. The solvents used in printing may be low molecular weight organic compounds consisting of alcohols, hydrocarbons, glycol ethers, ketones, and esters (Robertson 1993). The compounds involved in flavor degeneration of a

product from the ingress of adhesives and organic solvents used printing inks usually contain four to twelve carbons and may often contain several functional groups (Strandburg and others 1991).

The residual compounds migrate through into the product headspace or the product itself. The odor threshold of the human nose for many of these volatile compounds is well below the levels at which they are toxicologically significant. Therefore, there is a health risk if the solvent compounds used during printing are retained at toxicological levels. However on a more practical level, the larger issue of off-odor and off-flavor development and their affect on food product quality is the concern. This is because off-odors develop at retained solvent levels that are much lower than levels that pose a health threat. Current trends in the food industry indicate a widespread emphasis on product quality, and the monitoring of any potential source of off-odors is a concern.

The sensory odor thresholds for ethyl acetate, toluene, and a variety of aldehydes and ketones were found to range from parts per million to the parts per billion level (Halek and Hatzidimitriu 1988). A major cause of high retained-solvent levels is inadequate drying during lamination or after printing. The amount of solvent compound that ends up in the food product is dependent on the partition coefficient for that compound, package, and product. The partition coefficient denotes the division of the total amount of the solvent compound between the package and the product. These coefficients were determined by Halek and Hatzidimitriu (1988) for six printing ink solvents (ethyl acetate, hexane, isopropanol, 2-methyloxyethanol, methyl ethyl ketone, and toluene) in chocolate liquor, high fat cookies, and soybean oil. The highest coefficients, or product with the highest concentrations was the soybean oil, with the product having the lowest concentrations being the cookies. High fat content products, such as chocolate, are more likely to absorb foreign volatiles or odors than other food products.

A plasticizer is a compound that is added to materials to increase their flexibility. In polymer packaging in the food industry, plasticizers are used in both the polymer films themselves as well as in the inks used to print on films. Organic solvents are used in adhesives used in laminating multiple layers in polymer packaging. These compounds, if they remain at sufficient concentrations on the films after processing, may potentially migrate through the packaging and interact with the food product.

Most plasticizers used in polymer films are phthalate compounds, which are esters of phthalic acid and have a variety of long chain alcohols. Esters of adipic acid are also used. The most commonly used phthalate ester is di-2-ethylhexyl phthalate (DEHP). DEHP, diethyl phthalate (DEP), and di-isooctyl phthalate (DIOP) have been granted sanction for used by the Food and Drug Administration (FDA) for food with high water content only, while other phthalate esters have been cleared to be used as plasticizers in materials for various food contact uses. It should be noted that only minor amounts of plasticizers are used in commercial printing inks and subsequently only extremely low levels migrate into the food product (Page 1988; Katan 1996, Metcalfe and others 1997).

DEHP is a demonstrated carcinogen in rats and mice, although the effects of DEHP consumption on human health have yet to be determined (Page 1988). According to the FDA, a component of a food packaging material is subject to definition as a food additive if it may reasonably be expected to become part of the product or to affect its characteristics, directly or indirectly. In addition, no additive will be recognized as safe if it is found to induce cancer in man or animal. Because DEHP is a demonstrated carcinogen, other phthalate compounds similar in structure are also in question and of immediate concern. Again, the issue of concern is the toxicity of additive chemicals at the concentrations found in the food product not the concentrations found in the packaging material. So the focal point becomes to what extent the plasticizers and other questionable compounds migrate into the food product. Page and Lacroix (1992) found that DEHP migrated from a paper-foil package to the product in concentrations up to 11.9 μg/kg. A survey performed Harrison in 1998 in the United Kingdom estimated the dietary intake of plasticizers due to migration from packaging to be less than 2 mg per day. In the United States, the FDA is currently exploring the implementation of threshold regulations for migratory compounds (Robertson 1993).

In a study performed in 1989 by Castle and others, it was demonstrated that on polypropylene packaging, transfer of components from the ink on the outer surface of the film on the inner food contact surface occurred amounting to 6% of the total amount of plasticizers used in the printing system for dicyclohexyl phthalate. Plasticizers are widely used in plastic films and coatings and are also used in printing inks. The plasticizers used in the ink printed on the outer surface of the packaging material are usually used at levels from 2% to 8%. They form an essential part of the printing ink formulation and contribute to the adhesion of the ink to the

package. Plasticizers that are frequently used in such a manner include dibutyl, dicyclohexyl, and di(2-ethylhexyl) phthalate esters. In the same study, it was found that in each case of retail food samples that were tested, blank foods had negligible plasticizers levels and the packaged foods had plasticizers levels corresponding to those found in the packaging material (Castle and others 1989). The results of a study conducted by Nerin and others in 1993 support these findings and also found new plasticizers such as N-ethyl-toluene-sulphonamide, which is used as a substitute for phthalate plasticizers in printing inks. The plastics examined in these studies were oriented polypropylene that does not require the use of plasticizers to achieve the desired plasticity. Consequently, the migrating plasticizers that were studied came only from the printing inks used on the films (Nerin and others 1993).

In the study performed by Nerin and others in 1993, the plastic packaging films and their printing inks were analyzed using gas chromatography, gas chromatography-olfactory, and gas chromatography – mass spectroscopy. While these methods are useful research tools, they require extensive time and preparatory measures that make them impractical as sole effective measures in quality control. As an alternative measure, the use of a chemosensory system or electronic nose has been introduced as a means to classify and characterize films and has the potential to be useful tool in quality control.

**Migration**

Migration is a two-way process whereby a product may be altered by either having components leave or be 'scalped' into the packaging material, or by having components of the packaging material migrate into the product itself. A third possibility involves the diffusion of compounds from the environment surrounding the packaging through the packaging and into the product.

Diffusion is the primary mechanism for the transfer and migration of chemical compounds from the packaging materials to food. Free volume theory, which asserts that the molecular motion in the bulk state occurs due to the presence of holes or vacancies, and concentration potential are the most prevalent theories explaining the diffusion of molecules through solid materials (Ozdemir and others 1999).

Fick's second law can be used to describe the migration of a compound from a polymer film to a food product. This law may be organized as shown in Equation [1] to describe the amount of compound, $m_t$, migrating from the film to the food across surface area, A, and over

time t (Robertson 1993). The migration of organic volatiles through multilayer packaging is considered as migration through membranes in series.

$$Jt = \frac{m_t}{A} = 2c_{Po}\left[\frac{\beta}{1+\beta}\right]\left[\frac{D_P t}{\alpha}\right]^{\frac{1}{2}} \qquad [1]$$

where

$$\beta = \frac{1}{K}\left[\frac{D_F}{D_P}\right]^{\frac{1}{2}} \qquad [2]$$

J = diffusive mass flux, $kg \bullet m^{-2}s^{-1}$

t = time, s

$m_t$ = mass of permeant passed through area A during time t, kg

A = cross-sectional area, $m^2$

$c_{Po}$ = initial concentration of the migrant in the polymer film, $kg \bullet m^{-3}$

$D_P$ = diffusion coefficient for the polymer film, $m^2s^{-1}$

$\alpha$ = ratio of mass of permeant to the mass of the membrane, dimensionless

$D_F$ = diffusion coefficient for the food product, $m^2s^{-1}$

K = partition coefficient that gives the ratio of the concentration of the migrant in the polymer to the concentration in the food at time t, dimensionless

The permeability of the packaging materials to organic vapors is important in retaining desirable flavor volatiles within the package, or from inhibiting undesired components to permeate through the package from within the package itself or its surrounding environment. The permeation rates of gases and water vapor through types of polymer films are well known. Also, there is a great need for data regarding the permeation rates of organic volatiles through polymer films.

Additives are used in the production of plastics in food packaging to enhance their physical properties. These additives tend to migrate from the plastics due to their high mobility and low molecular weights. Possible migrants from plastics could be monomers, oligomers, plasticizers, antioxidants, antistatic and antifogging agents, colorants, emulsifiers and degradation products. Some plasticizers, which function to add softness and pliability to the plastic, that are of particular concern include phthalates and adipates. Sources of compounds that

may migrate into food from plastic films can be ink solvents, adhesive systems used in laminations, and polymerization reactions in which a solvent is used as a reaction medium. Migrating solvents such as abietic acid, toluene, butanone-2, ethyl acetate, and hexane are also of concern as well as pigments such as molybdate orange (Ozdemir and others 1999).

Gilbert and Others (1988) demonstrated the use of a feasible analytical approach using a method called stable isotope dilution GC-MS to assess the levels of most organic compounds that may migrate into products in commercially produced materials.

**Printing**

Most plastic packaging used in retail is printed. Polymer films such as polypropylene, polyethylene, polyesters, and ethylene/vinyl acetate copolymer cannot be printed on without pre-treating the surface of the films to obtain adequate adhesion between the inks used and the plastic. This is pretreatment is needed because the non-polar, inert nature of the plastic itself inhibits any chemical or mechanical bonding with the ink (Robertson 1993). Through cleaning and various process treatment, the surface of these plastics are activated and become more polar and subsequently a more readily printable surface. Dependent upon the graphic resolution of the marketing design for a printed package, the length of the printing run, and the geometrical shape of the packaging material to be printed, several printing methods are available for commercial printing. Offset lithography, a method that is rarely used to print on plastic films, is a method often used to produce high quality printing on papers. The two primary printing techniques used to prepare polymer film packaging in the food industry are the flexography and roto-gravure methods.

Flexography, a form of letterpress or relief printing, is a widely used direct rotary printing process used in food packaging. Cylinders are formed from photopolymer plates using a label design initially developed in marketing. The label design is transferred to film negatives that are then used to create the photopolymer plates. Exposing the light sensitive photopolymers to UV light through the film negative, which exposes an image that then remains raised on the plate, forms the photopolymer plates. The plate is then mounted on a cylinder. One cylinder is produced for each color in a label design. Each color is individually printed and dried before the next color is printed, and the colors are printed over one another. Flexography as a high speed printing technique was initially developed in Germany and introduced commercially in the United States in the 1920s (Robertson 1993).

Roto-gravure, a form of intaglio printing, is also a widely used rotary printing process used on food packaging. The cylinders used in roto-gravure are usually prepared with a chrome-plated copper etched surface. The surface of the cylinder is etched with many small cells or pores that hold varying amounts of ink, depending on their depth, and produce the image as ink is drawn from the pores through contact with the polymer receiving surface. Consequently, it is a recessed image on the cylinders that is put upon the packaging material. The use of the roto-gravure method allows greater image resolution than images produced using the flexography printing method. The life of the cylinder, in terms of the number of impressions that may be produced with it, is also significantly greater than those used in flexography printing. However, the production of these cylinders requires considerably more time and they are more expensive to produce. Also, although each color is printed separately as in flexography, the requirements for drying and aligning each color as it is printed makes it necessary to have a separate station in a press for each individual color as it is printed.

Typical printing inks used in commercial presses contain ingredient classes that include pigments, a vehicle, solvents and additives. The pigments provide the color while the vehicle is the resinous component that binds the pigment particles and adheres them to the substrate surface. Significant efforts have been made in recent years to eliminate or reduce the used of compounds derived from heavy metals such as lead, mercury, bismuth, antimony, and cadmium, which are some of the most brightly colored and UV-stable ink pigment components. The solvents are used to dissolve the resins and fluidize the inks to decrease the viscosity of the ink formula. The additives include wetting agents, plasticizers, dryers, tackifiers, and other physical property modifying components (Soroka 1995). The inks solidify by the evaporation of the solvents, oxidation, or chemical reaction. Inks are generally formulated for specific substrates. Printing of polymer packaging for the food industry predominantly uses inks diluted with organic solvents.

Flexography requires less time and capital investment to produce the plates and mount them on the cylinders used to print a label and is generally the first choice when selecting a printing process. However, if the marketing design calls for resolution that is greater than can be met by using the flexography printing process, roto-gravure is often used. The decision as to which method to be used is generally made after the final label design from marketing has been decided upon.

Roto-gravure generally leaves more ink and ink solvents on the packaging during the printing process than does the process of flexography. Most gravure inks are highly volatile although they dry almost instantly (Long 1973). However, the foremost factor in determining the amount of ink residue left on a package from the printing process is the actual color requirements called for in the label design. The number of colors used and the percent coverage of each on a label impression that is required in a design strongly influence the amount of ink, and ink solvents used and left on packaging films during printing.

**Odor and Flavor**

The flavor of a food product is the integrated perception of a consumer using both the senses of smell and taste. Taste buds located on the tongue and in the back of the mouth enable a person to sense sweetness, sourness, saltiness, and bitterness. The tongue is also used to sense the physical texture of the food. Specialized cells of the olfactory epithelium within the nose are able to sense aroma volatiles. Together the human nose and tongue function together to assess and perceive the flavor of a product at the time of consumption.

Aromas are normally comprised of small molecules, light (< 300 Dal), polar and usually hydrophobic (Payne 1998). Simple aromas contain only one component. An example would be an alcohol. Complex aromas contain as many as hundreds of thousands of components. The commonly used example to demonstrate a complex aroma is coffee. Although coffee has a very distinct aroma, it is a complex with many components. The differences in aroma between different types of coffee are caused by subtle differences in components of a complex aroma (Payne 1998).

Aromas in the food industry, from raw ingredients to the final packaged product, are frequently important. These odors are currently monitored using sensory panel measurements and or through analytical techniques such as GC, GC/MS, and GC-olfactory. In recent years, electronic nose instrumentation has found expanded use as a complimentary tool to these techniques.

Off-odors and taints can arise in food products as a result of decomposition due to endogenous enzymes, microbial contamination, chemical oxidation, or other means of contamination (Hodgins and Simmonds 1995). Off-odors in food are one of the main reasons for consumer rejection of a product. One production run of a product with serious off-odors can

result in damaged market sales as consumers may not only reject the product but also never try the product again.

Microbial contamination can produce sulfur volatiles, amines, and chloroanisoles that cause putrid, ammonia-like, musty odors in a number of products. Chemical oxidation and enzyme decomposition usually lead to a range of rancid-like off-odors. This is particularly true in food products with high lipid levels due to the formation of aldehydes and ketones (Hodgins and Simmonds 1995).

**Sensory Evaluation and the Human Nose**

Well-trained sensory panels can detect aroma changes in a sample from subtle taints to major differences. The major limitations of sensory panels are their limited availability, associated costs, fatigue and time limitations, and inherent subjectivity.

The major advantage to the use of human sensory panels is that they are based upon the sensitivity and selectivity of the human nose that is currently the foremost tool for odor analysis. In addition, it is the method used by end-users in the final assessment of a product prior to consumption.

The food packaging industry is currently involved in measuring odors and taste as it relates the packaging material to the integrity of the food product. Sensory evaluation attempts to put a quantitative value on "Total Aroma Perception" and analyzes the concentration, potency, and hedonic value of an aroma (Hodges 1991). Current sensory analysis of packaging odors in the food industry commonly uses jar odor evaluations with triangle and/or Robinson tests. Essentially, packaging is heated in a sealed container for a specified amount of time and then the panelist punctures or opens the lid and makes an assessment of the odor. The odor is analyzed by rating it on a scale with a preset rating that is the fail point, or the sample that is different from the others given is identified. This method of analysis uses the human olfaction system as the sensory instrument.

The human olfaction system uses approximately 10,000 sensors in the nose to produce the signals that the brain interprets and recognizes as a particular aroma (Hodgins 1996). The human olfactory system is capable of detecting aromas from compounds at concentrations in the sub-ppb range (Payne 1998). The olfaction system involves sensing by the olfactory receptor cells, signal processing by the olfactory bulb, and signal recognition by the brain.

Proteins in the olfactory receptor cells located in the olfactory epithelium at the top of the nose interact with compounds in an aroma to cause the excitation of neurons. However, very little is known about the specific mechanisms involved in both the interaction of aroma compounds and receptor cells and the manner of signals produced by excited neurons. Receptor sensors may send individual signals to the brain, or by a number of grouped sensors may be grouped may produce a smaller number of signals sent to the brain. The end result is that the human brain and 10,000 receptors in the nose function together to respond to and recognize complex vapor aromas. There are numerous theories about the response mechanism of the sensor receptors in the human nose. One theory suggests that resonating nose receptors are excited by vibration modes in the vapor molecules. Another theory suggests that the vapor molecules fill gaps or holes in specific receptors in the nose altering their conductance to induce a sensor response. However, these theories only speculate on possible mechanisms and no theory has been proven to date to explain the receptor mechanisms of the human nose. It is generally accepted that the human sensors are nonspecific and highly sensitive (Hodgins 1996).

It is not known exactly what the human nose responds to in an aroma, nor the mechanism of the response. Therefore, it is not possible at this time to develop equipment that can be used continuously for long periods of time at low costs that correlates completely and totally with the human nose.

**GC/MS**

Analytical techniques such as gas chromatography and mass spectroscopy can be used to monitor and identify compounds and their concentrations in an aroma. However, the results from these techniques are not in a form that can be directly related to odor information obtained by a human sensory panel (Hodgins and Simmonds 1995). Consequently, headspace GC-MS analyses are often used in 'trouble-shooting' and preliminary quality inspections. The high demand for on-line and in-process controls to maintain product quality has resulted in the use of GC and GC-MS techniques to monitor processes and sensory panel analysis is generally relegated to product research and development and the start and end of a production process (Strassburger 1996). Correlating and coordinating the results of GC analysis to sensory scores is difficult. An alternative method, GC-olfactory, allows a human panelist to sniff aromas from individual compounds in a more complex mixture. This is useful in determining what components contribute significantly to the overall odor of a complex mixture. GC-olfactory

techniques offer a method that is able to bridge the gap between the human nose and analytical techniques to some degree, but finds major difficulties in the practicality of its use. The true aroma of a sample is result of the complex interaction of all volatile compounds within the product sample not the individual components themselves. Also, sound statistical experimental designs have extensive time requirements and require either multiple sniff ports or multiple GC-olfactory units.

**Electronic Nose Overview**

Electronic noses are gas multi-sensor arrays that are able to measure aroma compounds in a manner that is closer to sensory analysis than gas chromatography. They are instruments comprised of an array of partially specific chemical sensors and pattern-recognition information processing system that is capable of recognizing complex aromas. Electronic noses are comprised of (1) chemical sensors that are used to measure aromas, (2) electronic system controls, and (3) information processing systems for aroma identification. Although there are various sensor technologies used among the current manufactured instruments, most systems work using the same series of steps. They analyze compounds in a complex aroma and produce a simple output.

The steps involved include: (1) generating an odor from a sample, (2) exposing the sensor array to the aroma, (3) measuring changes in an array of sensors when they are exposed to the odor, (4) establishing a recognition pattern for the sample from the responses of all or a number of sensors in the system, and (5) using this information in statistical analyses to compare to a database of other chemosensory measurements.

An aroma may be taken at ambient conditions to mimic what the human nose would experience under normal circumstances or the sample may be heated to intensify aroma concentrations. Aroma exposure to the sensor array is generally accomplished by one of two methods: static headspace analysis, and flow injection analysis. Static headspace analysis involves direct exposure to a saturated vapor taken from the headspace above a sample. Flow injection analysis involves injecting the aroma sample into a control gas that is constantly pumped through the sensor chamber (Payne 1998).

**Electronic Nose History**

In recent years, there have been major advances in sensor technologies for odor analyses. Electronic noses have been around for approximately 35 years, and the last fifteen years have

seen dynamic advancements in both sensor technology and information processing systems. Chemosensor array based systems using the conducting polymer technology were initially developed in the early 1980s (Payne 1998). Initial work on electronic nose with this technology stemmed from polymer development technology achieved by the US Air Force. The Air Force was attempting to use certain polymers found to conduct electricity to build an airplane that would better evade radar. Researchers at Britain's Warwick University in the mid-1980s used the findings from the military research to develop the first electronic nose chemosensory system based on conducting polymer sensors (Pope 1995). Since that time other new sensor technologies have been developed that have properties more suitable for particular applications.

Metal oxide semiconductor gas sensors were first used in the 1960s in Japan in home gas alarms. The conducting ceramic or oxide sensors were invented by Taguchi and produced by the company Figaro (Schaller and Bosset 1998).

Electronic nose instruments have been tested successfully for use as a complimentary tool in the discrimination of many consumer products.

**Electronic Nose Niche**

The electronic nose has both advantages and disadvantages over the use of human sensory panels as well as GC/MS analyses. Therefore, it finds use as a complimentary instrument to monitor odors.

The human olfaction system, which is the basis of sensory panels, is still the most sensitive device available for aroma measurement. It is also the odor measurement method used by consumers when assessing the odor of consumable products. Therefore, it is important that any odor monitoring methods used in quality control or quality assurance be capable of detecting odors that may be found to be offensive by the human olfactory system. This fact is also the reason that human sensory panels are still the basis of aroma measurements in the food industry.

Although electronic noses cannot compete with the sensitivity and final correlation of sensory panels, they are objective instruments and involve primarily a capital investment. They can also be used on the production floor. Work performed by Strassburger (1998) demonstrated that an MOS sensor based instrument showed great potential in aiding in flavor analysis going from the research and development phase to the production floor as it produced results that were directly correlated to sensory and analytical results.

Sensory panels are inherently subjective and the physical condition of panelists may vary from one day to another. This brings inherent error into any scientific quantification of experimental results. Human panels require sustained training for each type of product or sample and standardization between different panels at different sites is extremely difficult. Sensory panels have high costs associated with training, maintaining, and testing, and they experience fatigue. Therefore, they are not run continuously for extended periods of time. A trained electronic nose provides a complimentary objective tool available for 24-hour complex aroma analysis (Payne 1998). Newman and others (1999) used a conducting polymer sensor based electronic nose as a complimentary tool to sensory analysis in the odor analysis of raw tuna quality. Electronic nose measurements were successfully correlated with sensory scores with correct classification rates of 88%, 82%, and 90% for raw tuna stored at three temperatures.

The electronic nose is an instrument that can be either portable or be connected to an auto-sampler to reduce the need for human involvement in multiple sample testing. It is also an instrument available to potentially test odors that a human sensory panel would not be willing to test, although this facet is not particularly pertinent to the food industry.

Past objective odor monitoring analyses options involved either the use of analytical GC/MS techniques. These techniques offer identification and quantification of compounds comprising an aroma. However, GC/MS techniques often find difficulties in identifying which of the comprising compounds contribute to the recognized odor and to what extent, particularly if they are complex odors. Electronic noses have a unique advantage over GC and MS techniques because it is an analytical technique that samples an entire aroma rather than identifying it by its comprising components. It is also a faster method of aroma analysis (Payne 1998). A portable electronic nose unit could also be used to directly sample headspace aromas from bulk raw materials or food containers where sampling for GC/MS analysis becomes difficult (Hodgins and Conover 1995).

Electronic nose analysis is also a technique that may be non-destructive and incurs low operational costs. Overall, it fills a number of gaps in odor analysis not achieved by use of sensory panels and GC/MS techniques in conjunction. While the electronic nose has a number of weak points that inhibit its ability to be used exclusively, it is a powerful tool that enhances aroma monitoring when used as a complimentary tool to sensory panels and GC/MS techniques.

**Electronic Nose Market**

The market for electronic nose instrumentation has been developed as a result more of 'technology push' rather than 'market pull' (Payne 1998). The technology has been continually developed without an existing market demand and manufacturers have actively pushed sales and pursued applications in which electronic nose instruments would be useful. There are numerous and expanding applications in which such an instrument would be complimentary and enhance a product or process. As a result of this market situation, manufacturers are able to offer strong product support and aid in the implementation of their instrument. However, until the recent development of portable electronic noses, long research development and associated costs have resulted in high pricing of most electronic nose systems. This has in turn retarded their expansion into new applications. End-users are hesitant to purchase these instruments without being fully assured that it will work as the manufacturers claim. The production of an industrial electronic nose that is reliable is still in the development phase, and most systems currently available are most suited to a laboratory environment (Payne 1998).

Current commercial electronic nose system manufacturers that are most involved in the market include: Airsense (Germany), Alpha MOS (France), Applied Sensor (US) * merged from Nordic Sensor Technologies (Sweden) and Motech GmbH (Germany), AromaScan (UK), Bloodhound Sensors (UK), HKR Sensorsystems (Germany), Lennartz electronic (Germany), Neotronics (USA, UK), RST Rostock (Germany), and OligoSense (Belgium) (Payne 1998).

The four major types of chemosensory based electronic nose technology include metal oxide semiconductor sensors, conducting polymer sensors, quartz microbalance sensors, and metal oxide field effect transistors. Certain manufacturers in recent years have also been developing hybrid or modular chemosensory systems that use multiple sensor types. The MOS and MOSFET sensors are considered to be 'hot' sensors and the remaining sensor technologies, CP and QMB sensors, are considered to be 'cold' sensors due to their operating temperatures (Schaller and Bosset 1998).

MOS sensors and conducting polymer sensors are the two technologies that have been used the longest in commercial electronic nose systems. Conducting polymer sensors are easily fabricated and are fabricated with a high degree of reproducibility. They also have the greatest range of selectivity and sensitivity. However, the MOS based systems are less susceptible to water vapor variations, are more robust, have a longer useful life, and are cheaper to replace.

**Metal-Oxide Sensors**

Metal oxide semiconductor (MOS) sensors consist of a ceramic substrate heated by wire and coated by a metal oxide semiconducting film. The metal oxide coatings used are often n-type oxides that include zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide. P-type oxides such as nickel oxide or cobalt oxide are also used.

The main difference between sensors using the two types of oxide coatings are the types of compounds with which they react. The sensors using n-type (n = negative electron) coatings respond to oxidizing compounds because the excitation of these sensors results in an excess amount of electrons in its conduction band. The p-type (p = positive hole) sensors develop an electron deficiency when excited and therefore are more prone to react with reducing compounds (Schaller and Bosset 1998).

MOS sensors have a low sensitivity to moisture and are robust. They typically operate at temperatures ranging from 400 °C to 600 °C to avoid moisture effects. These sensors are not typically sensitive to nitrogen- or sulfur- based odors, but are sensitive to alcohols and other combustibles (Bartlett and others 1997).

**Conducting Polymer Sensors**

Conducting polymer sensors are composed of a conducting polymer, a counter ion, and a solvent that are grown from a solution onto an electrode bridging a 10-μm gap to produce a resistor. Measurements are made by measuring changes in resistance. Altering one or more of the three comprising materials produces different sensors. The single stage fabrication technique allows the reproducibility from the production of one sensor to the next to be consistent.

Conducting polymer sensors are formed electrochemically onto a silicon or carbon substrate. This results in a polymer in an oxidized form that has cationic sites and anions from the electrolyte. Sensors made from polymers based on aromatic or heteroaromatic compounds, such as polypyrrole, polythiophene, and polyaniline, are sensitive to many volatile compounds and experience a reversible change in conductions (Persaud and others 1999). Conduction is achieved in the electrically conductive polymer by electron transport, not ion transport. The charge is carriers are associated with the cation sites (Hodgins and Simmonds 1995).

Although the conducting polymer sensors have the greatest range and balance between selectivity and sensitivity, they are more sensitive to water vapor and are more expensive to produce and replace. They can be used at room temperatures and temperatures moderately

higher. This allows for future development of handheld electronic nose instruments and avoids problems associated with the breakdown of volatiles at the sensor surface of systems using increased heating (Persaud and others 1999).

**Quartz Microbalance**

Quartz Microbalance (QMB) sensors, or Quartz Crystal Microbalance (QCM), are sensors that evolved from a larger group of piezoelectric crystal sensors. These sensors use crystals that can be made to vibrate in a surface acoustic mode (SAW) or bulk acoustic mode (BAW). The sensors are made from thin discs composed of quartz, lithium niobate ($LiNbO_3$), or lithium tantalite ($LiTaO_3$) and then coated. The coating materials are usually gas chromatographic stationary phases but may be any non-volatile compounds that are chemically and thermally stable (Schaller and Bosset 1998).

The quartz microbalance sensors respond to an aroma through a change in mass. When an alternating voltage is applied at a constant temperature, the quartz crystal vibrates at a very stable and measurable frequency. This is dependent upon the assumption that viscoelastic effects are negligible (Bartlett and others 1997). Upon exposure to volatile compounds in an aroma, the volatiles adsorb onto the GC phase coating of the sensor, which causes a change in the mass of the sensor. The change in mass results in a measurable change of the oscillating frequency of the sensor. QMB sensors have developed as a useful electronic nose technology because of they produce stable responses and are formed through a simple fabrication process.

In reporting on trends and developments in quartz microbalance chemosensory systems, Nakamoto and Morrizumi in 1999 performed work examining QMB sensor responses with different aroma injection systems as well as model development for response prediction. QMB sensor technology continues to improve and Applied Sensor has released a handheld unit this year that is currently the least expensive electronic nose system on the market.

**Metal Oxide Semiconductors Field Effect Transistors (MOSFET)**

MOSFET sensors respond to aroma volatiles with a measurable change in electrostatic potential. Each sensor in a MOSFET system consists of three layers including a silicon semiconductor, a silicon oxide insulator, and a catalytic metal. The catalytic metal component is also called the gate and is usually palladium, platinum, iridium or rhodium (Schaller and Bosset 1998). The standard transistor is an example of an “active” circuit component, a device that can amplify, producing an output signal with more power than the input signal.

The field-effect transistor (FET) controls the current between two points but does so differently than the bipolar transistor. The FET operates by the effects of an electric field on the flow of electrons through a single type of semiconductor material. Current flows within the FET in a channel, from the source terminal to the drain terminal. A gate terminal generates an electric field that controls the current.

Placing an insulating layer between the gate and the channel allows for a wider range of control (gate) voltages and further decreases the gate current (and thus increases the device input resistance). The insulator is typically made of an oxide (such as silicon dioxide, SiO2). This device is the metal-oxide-semiconductor FET (MOSFET). MOSFET sensors are similar to MOS sensors in that they are also robust and have a low sensitivity to water.

**Other Issues**

Issues such as sensor drift and the nature of the instruments discriminatory ability are major concerns as electronic nose technology is selected and developed for particular applications. To achieve the necessary repeatability, it is necessary that the sensors in the electronic nose systems react reversibly with the compounds in a sample aroma. Sensor drift occurs when the sensors experience small additive changes over time and usage. The aging of sensors, or sensor drift, has been a major issue of concern throughout the history of the development of electronic nose systems. However, some of the most recent advancements in electronic nose technology have been developed to deal with this issue. Advances in design and manufacturing of sensors have to increase the useful life of sensors, and calibration standards and artificial neural networks have been better developed to increase the reliability and longevity of measurements that unknowns are compared to. In addition, optimization of system and experimental parameters can establish more stable conditions and combat sensor drift. Mielle and Marquis (1998) performed work examining several parameters or dimensions of electronic nose analysis including sensor temperature, number of sensors, and sample incubation time, in order to stabilize system response and lengthen the useful life of library patterns in the system database.

The discriminatory power of any electronic nose chemosensory system is based upon its ability to respond measurably and repeatedly to components of aromas and to respond differently to aromas with varying components. The chemical nature and concentration of the volatiles in an aroma, reaction kinetics and dynamics of those volatiles, as well as system parameters and

sample preparation affect the fundamental response of each sensor. Schaak and others (1999) examined the effects of the system parameters; injection volume, incubation time, and incubation temperature, and their effect on sensor response and discriminatory power for the MOS sensor based Alpha M.O.S FOX 3000. Optimizing the system response of sensors in an electronic nose system through controlling system and experimental parameters is key to it being a useful analytical tool in most applications. Nakamoto and Morrizumi in 1999 reported that the QMB sensor responses could be predicted using computational chemistry. This allows for the ability of optimal sensor selection for target odors. Hansen and Wiedemann (1999) performed optimization work in using the Alpha M.O.S. (Toulouse, France) FOX 4000. The experimental and system parameters were investigated to optimize the response range of the sensors and enhance their discriminatory power. This work was performed using a full factorial design and examined four experimental parameters, incubation time, incubation temperature, sample mass, and sample agitation rate. It was found in this work that only the oven temperature had a major influence on volatile generation in the sample headspace. Bazzo and others in 1999 performed optimization work for the MOS sensor based FOX 4000 system in analyzing high-density polyethylene (HDPE) packaging. The optimization work allowed the selection of discriminating sensors as well as appropriate sample throughput conditions.

It is necessary to optimize electronic nose instrumentation to ensure sensitivity at the lowest detection thresholds. The threshold detection levels of 30 food aroma compounds with varying chemical structures for a MOS sensor based electronic nose system were found to be similar to reported ortho-nasal human detection thresholds (Harper and Kleinhenz 1999). Harper also found that the matrix solution used strongly influences electronic nose threshold levels and the use of a 4% ethanol matrix solution resulted in the sensor response resistance changes above their useable range. Subsequently, it is necessary to find a workable range of sensitivity for the sensors in a chemosensory array for particular samples in order to achieve an appropriate sensor response. It must also be acknowledged that although electronic nose technology continues to improve, it still responds very differently to many compounds than does the human nose. For example, the human nose is not sensitive to water vapor as well as several other compounds. However such compounds affect most electronic nose systems, particularly those operating at lower temperatures. Consequently, electronic nose systems may be blinded by such compounds or not suited to discriminating others that the human nose is sensitive to.

**Response Surface Analysis**

Problems exist with the use of electronic nose sensors such as sensor drift and poor repeatability and reproducibility due to system sensitivity to changes in operational conditions or poor gas selectivity and sensitivity (Roussel and others 1998). In order to overcome these difficulties, it is necessary to develop a successful and efficient testing methodology at optimum parameter settings. Roussel and others in 1999 examined the influence of various experimental parameters on the multi-sensor array measurements using an electronic nose with $SnO_2$ sensors and attempted to quantify them. Volatile concentration in the headspace increased as the sample temperature is increased. In screening factorial experimental designs, it is necessary that the response of the experimental parameters be monotonic within a studied range. Alternatively, response surface designs must be generated in order to develop a model of the multi-sensor response.

Response surface analysis involves the investigation of linear and quadratic effects of two or more factors. The fundamental principle of response surface methodology is to develop a simple mathematical expression, usually first- or second-order polynomials, that approximate the relationship between response and the examined factors (Devineni and others 1997). An experimental design is selected that allows a minimal number of experiments be used to examine a full range of values for a particular factor. Popular Box-Behnken designs are fractions of $3^N$ designs used to estimate a full quadratic model in N factors. They consist of all $2^k$ possible combinations of high and low levels for different subsets of the factors of size k, with all other factors at their central levels; the subsets are chosen according to a balanced incomplete block design for N treatments in blocks of size k. A number of center points, with all factors at their central levels, may also be added (Box and Draper 1987; SAS System Help 1988). The response surface analysis procedure uses the method of least squares to fit quadratic response surface regression models. The models focus on characteristics of the fit response function and in particular, where optimum estimated response values occur.

**Multivariate Factor Analyses**

Statistical analysis is key to understanding the sensor responses in an electronic nose instrument and realizing their discriminatory power. Discrimination and identification of sample recognition patterns requires the use of multivariate factor analysis. Factor analysis is a type of multivariate analysis that is concerned with the internal relationships of a set of variables

(Lawley and Maxwell 1971). There are several multivariate statistical methods used among electronic nose systems.

Multivariate Discriminant Analyses and PCA are factor analyses methods that are most common to electronic nose data analysis software and will be the primary discussion topics. Other types of factor analysis, such as cluster analysis, partial least squares, Soft Independent Modeling of Class Analogy, and Artificial Neural Networks will also be discussed briefly. Great length will be given to discussion of the descriptive statistics quantifying the amount of separation between sample classes and identification of unknowns, particularly the Mahalanobis distance.

**Principal Components Analysis**

Principal Components Analysis (PCA) allows data exploration and was initially developed and proposed by Hotelling in 1933. It is the extraction of principal factors through the use of a component model. This analysis process does so by assessing the similarities between samples and the relationships between variables. It is a linear technique and uses the assumption that response vectors are well described in Euclidean space (Bartlett and others 1997). The object is to determine if samples are similar or dissimilar and can be separated in homogenous groups and to determine which variables are linked and the degree to which they correlate. PCA summarizes information contained in a database in subspaces with the object of reducing the number of variables and eliminating redundancy (Gorsuch 1983; Jolliffe 1986).

In PCA, the principal factor method is applied to a correlation matrix with unit values as the diagonal elements. The factors then give the most suited least squares fit to full correlation matrix, with each factor ranked based upon the amount of the total correlation matrix that it accounts for. The principal components of the analysis are linear combinations of the original variables and the discerned information from the analysis are presented in two or three dimensional spaces relative to the chosen components, which are classified based upon the level of information that they produce. The smaller factors are generally dropped from the model because they carry a trivial portion of the total variance and do not provide significant information (Gorsuch 1983; AlphaSoft Manual 2000). PCA is a form of dimension reduction factor analysis where the relationships of a set of quantitative variables are examined and transformed into factors based on the amount of contributed variability to the system. Although PCA does not ignore covariances and correlations, it concentrates on variances. The principal

components are selected and ranked based on the amount of total variation, not the variation that most discriminates among classes of observations. This method of analysis is commonly used to reduce the number of variables used prior to performing discriminant analysis in order to make the calculations in the latter more manageable (Jolliffe 1986).

*Discriminant Analyses*

Multivariate discriminant analysis, also known as discriminant function analysis, discriminant factorial analysis (DFA), Gaussian discriminant function (GDF) and canonical discriminant analysis (CDA), originated with the work of Spearman (1904, 1926) and is the most common analysis method used by electronic nose systems to separate classes of observations in a database (Lawley and Maxwell 1971).

CDA may be used to determine descriptive variables that predict the divisions between groupings when information regarding sample groupings is known ahead of time. An algorithm is used to determine linear combinations of new descriptive variables that separate the predetermined groups as much as possible. A set of data $N_x$ is partitioned into m subsets $\{N_x^1, N_x^2, \ldots, N_x^k, \ldots, N_x^{m-1}, N_x^m\}$ that represent different quality descriptors. CDA proposes to then develop an algorithm with new variables $\{F^1, F^2, \ldots, F^j, \ldots, F^s\}$ that correspond to the directions that separate the subsets. This method allows the classification prediction of an unknown as one of these groups through the computation of the distance to the centroid of each of the groups. The unknown is classified with the closest associated group (Lawley and Maxwell 1971; Harman 1976; AlphaSoft Manual 2000).

CDA is a dimension-reduction type of factor analysis related to principal component analysis and canonical correlation. The manner in which the canonical coefficients are derived parallels that of a one-way MANOVA. In a CDA, linear combinations of the quantitative variables are found that provide maximal separation between the classes or groups. Given a classification variable and several quantitative variables, this procedure derives canonical factors, linear combinations of the quantitative variables that summarize between-class variation in much the same way that principal components summarize total variation. The discriminant function procedure in the SAS Software (Cary, North Carolina), PROC DISCRIM, develops a discriminant criterion to classify each observation into one of the groups for a set of observations containing one or more quantitative variables and a classification variable defining groups of

observations. The derived discriminant criterion from a training or calibration data set can be applied to an unknown data set (Harman 1976; SAS System Help 1988).

In CDA, the classification of an unknown observation involves plotting the unknown observation and determining if the point falls near the mean point of one of the groups. If the unknown observation is close enough, the sample can be classified as being the same material. If the point is far away from all groups in a database, the sample may be a different material or have a different concentration from the sample observations used as the training set data. The approach is relatively straightforward except for the concept of how being near a group is actually defined. Visual inspection of a CDA projection plot provides useful initial information. However, it is not a viable method for real world discriminant analysis applications. Quantification with a mathematical equation is needed to measure the closeness of the unknown point to the mean point of the groups in a database.

The Euclidean distance is one such measurement technique. The unknown response can be used to in a formula to calculate the distance of the unknown point to the group mean point. This would be an acceptable method except for two facts. The Euclidean distance does not give any statistical measurement of how well the unknown matches the training set, and the Euclidean distance only measures a relative distance from the mean point in the group. The method does not take into account the distribution of the points in the group, as the variation along one axis is often greater than the variation along another axis. The training set group points tend to form an elliptical shape. However, the Euclidean distance describes a circular boundary around the mean point. The Euclidean distance method is not an optimum discriminant analysis algorithm, as it does not take into account the variability of the values in all dimensions (Jolliffe 1986; Marcus 2001).

Mahalanobis distance (D), however, does take the sample variability into account. It weights the differences by the range of variability in the direction of the sample point. Therefore, the Mahalanobis distance constructs a space that weights the variation in the sample along the axis of elongation less than in the shorter axis of the group ellipse. In terms of Mahalanobis measurements, a sample point that has a greater Euclidean distance to a group than another sample point, may have a significantly smaller distance to the mean if it lies along the axis of the group that has the largest variability (Jolliffe 1986; Marcus 2001).

Mahalanobis distances examine not only variance between the samples within a group, but also the covariance among groups. Another advantage of using the Mahalanobis measurement for discrimination is that the distances are calculated in units of standard deviation from the group mean. Therefore, the calculated circumscribing ellipse formed around the cluster of a class of observations actually defines a preset number of standard deviations as the boundary of that group (Jolliffe 1986). The user can then assign a statistical probability to that measurement. For relatively large samples and normality assumptions D/2 behaves like a normal multivariate z with standard deviation 1. In theory, D/2 can be examined to obtain an indication of the separation between samples and their estimated populations, and the probability of incorrect assignment. A D value of 5 would correspond to about five standard deviation separations which covers approximately 99% of a population given a multivariate normal distribution. Separation of groups quantified with a Mahalanobis distance greater than 5 would indicate very little overlap. In practice, the determination of the cutoff value depends on the application and the type of samples (Marcus 2001).

The Mahalanobis distance, expressed as $D^2$ or D, is consequently the statistic most often used in multivariate analyses to identify unknown samples and to quantify the probability that they belong to the identified class. Mahalanobis distance is the most appropriate measure of multivariate relationships when data are normally distributed, homoscedastic, and has equality among covariance matrices. Most software give a classification matrix of the Mahalanobis distances to each group centroid and identifies the sample as belonging to the group with the smallest distance (Jolliffe 1986).

The Mahalanobis metric in a minimum-distance classifier is generally used as follows. Let $m_1, m_2, \ldots, m_c$ be the means for the c classes, and let $C_1, C_2, \ldots, C_c$ be the corresponding covariance matrices. An unknown vector x is classified by measuring the Mahalanobis distance from x to each of the means, and assigning x to the class for which the Mahalanobis distance is minimum (Knapp 1998).

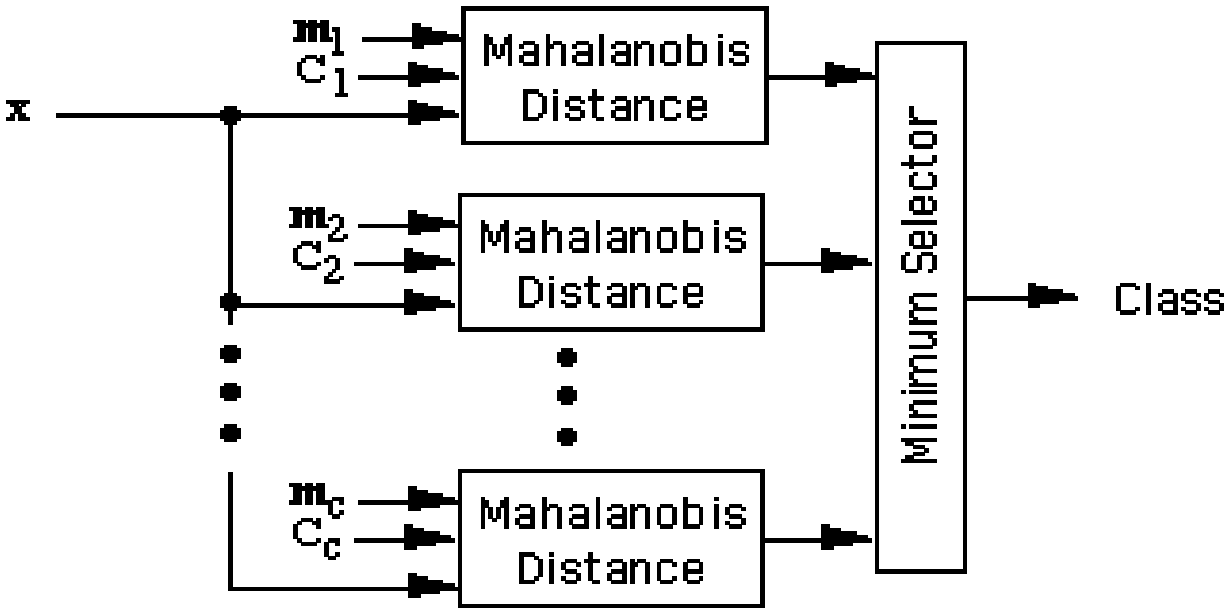



Figure 1. Mahalanobis minimum-distance classifier flowchart (Knapp 1998)

Articles are often not specific about reporting whether D or $D^2$ is being used, and usually it is only discerned in context. Mahalanobis D or $D^2$ is a descriptive measure of similarity or adjusting for pooled within variance and covariance. $D^2$ is calculated first and often preferred, as variance is often preferred to standard deviation, because of its additive and known distribution. Yet the only the standard deviation is in original measure units. Also, D is used as the ruler in canonical variate space or canonical projection plots and so is the more useful form when examining the data graphically (Marcus 2001).

$D^2$ is approximately chi-square distributed with p degrees of freedom. Therefore, an unknown is still assigned to the population with the smallest $D^2$. Furthermore using this idea, one can decide not to assign an unknown if all $D^2$ are larger than some cutoff based on the chi-square distribution with p degrees of freedom. It is also a useful statistic for finding multivariate outliers in a sample. If the data does follow a multivariate normal distribution, then the $D^2$ values will be approximately chi-squared distributed with p degrees of freedom. For standardized principal components, $D^2$ is the sum of squares (Jolliffe 1986).

One problem with the Mahalanobis Distance is that, because it is a summation of coefficient products, the number of observations and independent variables used in the calculation affects it. As with many multivariate quantitative methods, the Mahalanobis distance solves for multiple dimensions simultaneously. However, the Mahalanobis model tends to become over fit very quickly as more independent variables are added. This is similar to an

increased $R^2$ value for models when an increased number of independent variables are used and only logical when the method of calculating Mahalanobis matrix is considered. $D^2$ cannot be 0 as it is always a quantity greater than zero. Therefore $D^2$ is a biased estimate whether the null hypothesis is true or not. The size of the bias can be substantial when the sample sizes are small relative to the number of variables measured. An unbiased Mahalanobis distance ($D^2_u$) is given by Equation 3 (Marcus 2001):

$$D^2_{u(1|2)} = \frac{(n_1 + n_2 - p - 3)D^2}{(n_1 + n_2 - 2)} - \frac{(n_1 + n_2)p}{n_1 n_2} \qquad [3]$$

where

$D^2$ = Mahalanobis distance between classes 1 and 2, dimensionless

$n_1$ and $n_2$ = number of observations in class 1 and 2

p = number of independent variables

The answer to combining these apparently opposing necessities into one method for sample discrimination lies in first reducing the sensor data in electronic nose systems into its component variations with principal component analysis. A commercially available electronic nose, the Cyranose 320, uses this method in order to avoid over-fitting and instability in calculations. The PCA method indirectly performs a sensor selection and reduces the number of variables used in building a canonical model. It is recommended for that instrument that a breakpoint of 5 for the Mahalanobis distance, D, indicates well-separated groups (Cyranose 320 User's Manual 2000).

For cases where the number of observations or independent variables used in the discriminant analysis differ, it is not fair to compare Mahalanobis distances and so a standardized value must be compared. An average or unbiased Mahalanobis distance calculated by using a proportionality constant accounting for the number of independent variables and observations may be used or the F-value for the Mahalanobis distances may also be used for comparison as well. Hotelling's T-square, $T^2$, equals this distance except for an included proportionality constant. A problem with both $D^2$ and $T^2$ is that they are based on the inverse of the variance-covariance matrix, S = X'X, with the assumption that X has been centered and scaled. This inverse can be calculated only when the number of
variables, p, is small compared to the number of training set samples, N.

Mahalanobis $D^2$ is also part of the formula for finding the two-sample extension of student's t test, testing that the centroids of two multivariate populations have the same mean.

This is Hotelling's $T^2$ test, and is a maximum likelihood test. $D^2$ can be converted to $T^2$ and then to an F statistic, which has p, and $n_1$-$n_2$-p-1 degrees of freedom by multiplying by appropriate constants based on the number of observations in each class and the number of variables used. This statistic is known to be fairly robust to violations of normality assumptions, but is more sensitive to equality of variance assumptions, particularly for disparate sample sizes (SAS System Help 1988).

Because the F-value incorporates the Mahalanobis distance and also takes into account the number of observations used, the degrees of freedom, and the number of independent variables used, it is a useful term for comparing discriminant analyses performed by different systems. The Wilks' Lambda value is calculated from the inverse of the product of each of the eigenvalues incremented by one. Because Lambda is a type of inverse measure, values of lambda that are close to zero denote high discrimination between groups. The F-value for the Wilks' Lambda provides a quantitative value for the overall discrimination of all the classes involved in the discriminant analysis. While it is a useful number for quickly quantifying the amount of separation between classes, it denotes total discrimination and does not indicate if the total amount of separation is due to a balanced separation of all the classes or a very large separation of some classes while having little separation between other classes. Consequently, the most useful value in comparing Mahalanobis distances from different systems are the F-values for the Mahalanobis distances as they give a standardized value of the separation between each of the three classes analyzed in the discriminant analysis.

The percent correct during cross-validation also provides additional information regarding the degree of separation. After the discriminant model is developed, the most common method of validation is to use what is commonly referred to as the 'leave one out method' or cross-validation. In this cross-validation, each data point is removed and tested as an unknown to the model developed with the remaining data points. A value of 100% indicates complete separation of all classes. A value of 90% is usually considered sufficient validation for a database model. The user sets the actual required percent recognition for a training set validation based on the application requirements. This is also often called the "leave one out" procedure, as each observation is left out in turn in the analysis and then identified using all of the remaining data (SAS System Help 1988).

Equations 4-7a used to calculate the discussed terms are given as follows (Jolliffe 1986):

$$D^2_{(1|2)} = (\overline{x_1} - \overline{x_2})' COV^{-1} (\overline{x_1} - \overline{x_2}) \quad [4]$$

$$F_{Mahanalobis(1|2)} = \frac{(n_1 - 1) + (n_2 - 1) + (n_3 - 1) - p + 1}{(n_1 - 1) + (n_2 - 1) + (n_3 - 1)\, p} \frac{n_1 n_2}{n_1 + n_2} D^2 \quad [5]$$

$$\Lambda = \frac{1}{1 + \lambda_1} \frac{1}{1 + \lambda_2} \quad [6]$$

$$F_{\Lambda} = \frac{1 - \Lambda^{1/t}}{\Lambda^{1/t}} \frac{[N - 1 - 0.5(p+k)]t - 0.5[p(k-1) - 2]}{p(k-1)_1} \quad [7]$$

$$t = \sqrt{\frac{p^2 (k-1)^2 - 4}{p^2 + (k-1)^2 - 5}} \quad [7a]$$

where

$D^2_{(1|2)}$ = Mahalanobis distance between classes 1 and 2, dimensionless

$F_{Mahalanobis(1|2)}$ = F-value for Mahalanobis distance between classes 1 and 2, dimensionless

$\overline{x_1}$ and $\overline{x_2}$ = the geographic means of classes 1 and 2, dimensionless

$n_1$, $n_2$, and $n_3$ = number of observations in each class

p = number of independent variables

$\Lambda$ = Wilks' lambda, dimensionless

$\lambda_1$ and $\lambda_2$ = first and second eigenvalues derived from the discriminant analysis, dimensionless

$F_{\Lambda}$ = F-value for Wilks' Lambda, dimensionless

COV = pooled variance matrix, dimensionless

k = Number of classes

N = total number of observations in all classes

Other statistical analyses used include Partial Least Squares, Soft Independent Modeling of Class Analogy, Cluster Analysis, and the use of Artificial Neural Networks. Discriminant analysis should not be confused with cluster analysis and principal component analysis as discriminant analysis requires prior knowledge of the classes. The data used in cluster analysis do not include information on class membership. Its purpose is to construct the classification (Guertin 1970; SAS System Help 1988).

Partial least squares is a statistical method that may be used to extract quantitative information. It is an algorithm based on linear regression and can be used to extract concentration sensory score predictions. Partial least squares (PLS) is a statistical method that may be used to extract quantitative information such as concentration or sensory scores. The PLS algorithm, based on linear regression techniques, attempts to correlate a matrix containing quantitative measurements to a predictive matrix using a matrix of sensor measurements from the electronic nose instrument. After building the model, the predictive matrix is used to predict quantitative information contained in an unknown sample (Gorsuch 1983; AlphaSoft Manual 2000).

Soft Independent Modeling of Class Analogy (SIMCA) is a factor analysis method that is similar to PCA and CDA. This method classifies unknown samples using a comparison to a database composed of one group only. PCA is first performed on the data with the objective to find the subspace that most precisely contains samples. Each sample is explained in terms of its projection on the subspace and its projection on the orthogonal subspace. This matrix composed of a set of sensor observations induces two new matrices. The threshold identification criteria are set with theoretical values for the norm of the residual part of the predictive matrix and the Mahalanobis distance of the quantitative scores matrix to the centroid of the values projected in the subspace. SIMCA modeling works with as few as five observations from each population with no restriction on the number of independent variables (Jolliffe 1986; AlphaSoft Manual 2000).

Cluster analysis deals with data sets that are to be divided into classes when very little is known beforehand about the groupings. It provides an entry into factor analysis by establishing groupings within a data set. Within cluster analysis, principal components are calculated and used to provide an ordination or graphical representation of the data, or either to construct distance measures. The majority of cluster analysis techniques require the computation of similarity or dissimilarity among each pair of observations with the objective of clearly identifying group structures. The PCA graphical representation is often useful in verifying a cluster structure. This method of analyses is also often used in conjunction with artificial neural networks to perform the classifications (Guertin 1970; Jolliffe 1986).

*Artificial Neural Networks*

In many applications, there may be many references or combinations sensor data to which unknown needs to be compared. In these cases, an artificial neural network (ANN) is often used to analyze data from the sensor array. ANNs are particularly useful in analyzing data from hybrid electronic nose instruments where combined data must be analyzed. They are also particularly useful when the data to be analyzed exhibits a non-Gaussian distribution. The artificial neurons carry out a summation or other simple equation using predetermined weighted factors. The weighted factors are determined during the training of the neural network and are set arbitrarily before it is trained (Hodgins and Simmonds 1995). The training process for any ANN is a defining factor for its success.

The training of an ANN is accomplished by inputting data from the sensor array to the artificial neurons defined by a set answer for that data. The neural network calculates the values at all the neurons in the hidden and output layers. A back propagation technique is then used to adjust the weighted factors until the correct output is achieved. This is repeated for all sensor data for all samples in a training set. A common breakpoint value for determining if the ANN is sufficiently trained for an application is if the weighting factors vary by no more than 10% during a training run (Hodgins and Simmonds 1995).

A trained ANN can then be used to identify an unknown sample by comparing it to all of the references in the training set. In practice, ANNs do not always identify unknowns that are one of its references with 100% confidence. However, ANNs do provide a means for performing numerous comparison calculations quickly to provide identification.

**Conclusions**

Electronic nose instrumentation has potential to be an effective complimentary tool in the quality analysis of odors on printed films. It is an objective analytical technique that analyzes complex aromas and unlike sensory panels, it may be utilized 24 hours a day. If it can be established that such instrumentation has the sufficient sensitivity and selectivity to discriminate among retained solvent aromas, then correlation with human sensory panel analyses and gas chromatography analyses would provide useful additional information for quality control. Electronic nose instrumentation is a potentially powerful discriminatory tool for quality control analysis of retained solvent odors in plastic food-packaging films.

**References**

AlphaM.O.S. 2000. AlphaM.O.S. Introductory Manual. AlphaM.O.S. Toulouse, France.

Bartlett PN, Elliot JM, Gardner JW. 1997. Electronic noses and their application in the food industry. Food Tech 51(12):44-48.

Bazzo S, Loubet F, Labreche S, and Tan TT. 1999. Optimization of Fox sensor array system for QC packaging in factory environment. Robustness, sample throughput and transferability. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 225-144.

Begley TH. 1997. Methods and approaches used by FDA to evaluate the safety of food packaging materials. Food Add and Contam 14(6-7):545-553.

Box G, Draper NR. 1987. Empirical model-building and response surfaces. New York: John Wiley & Sons. 669 p.

Cardello AV. 1998. Perception of food quality. In: Taub IA, Singh RP, editors. Food storage stability. P 6-7.

Castle L, Mayo A, Gilbert J. 1989. Migration of plasticizers from printing inks into foods. Food Add and Contam 6(4):437-443.

Cyrano Sciences. 2000. Cyranose 320 User's Manual. Cyrano Sciences. Pasadena, CA.

Devineni N, Mallikarjunan P, Chinnan MS, Phillips RD. 1997. Supercritical fluid extraction of lipids from deep-fried food products. J Amer Oil Chem Soc 74(12):1517-1523.

Gilbert J, Castle L, Jickells SM, Mercer A, Sharman M. 1988. Migration from plastics into foodstuffs under realistic conditions of use. Food Add and Contam 5:513-523.

Gorsuch RL. 1983. Factor analysis 2nd ed. Hillsdale, New Jer: Lawrence Erlbaum Assoc. 425 p.

Guertin W, Bailey JP. 1970. Introduction to modern factor analysis. Michigan: Edwards Brothers, Inc. 472 p.

Hansen WG, Wiedemann SC. 1999. Evaluation and optimization of an electronic nose. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 131-144.

Harman HH. 1976. Modern factor analysis. Chicago: University of Chicago Press. 487 p.

Harper WJ, Kleinhenz JP. 1999. Factors affecting sensory and electronic nose threshold values for food aroma compounds. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 308-317.

Hernandez RJ, Giacin JR. 1998. Factors affecting permeation, sorption, and migration processes in package-product systems. In: Taub IA, Singh RP, editors. Food storage stability. P 289-293.

Hodges K. 1991. Sensory-directed analytical concentration techniques for aroma-flavor characterization and quantitation. In: Risch S, Hotchkiss J, editors. Food and packaging interactions II. Washington, DC: American Chemical Society. P 174-182.

Hodgins D, Simmonds D. 1995. Sensory technology for flavor analysis. Cereal Foods World 40(4):186-191.

Hodgins D. 1996. Electronic nose technology. Perfumer & Flavorist 21(3):45-48.

Hodgins D, Conover D. 1995. Evaluating the electronic NOSE. Perfumer & Flavorist 20(6):1-8.

Hotchkiss JH. 1997. Food-packaging interactions influencing quality and safety. Food Additives and Contaminants 14(6):601-607.

Jenkins WA, Harrington JP. 1991. Packaging foods with plastics. Lancaster, Penn: Technometric. 326 p.

Jolliffe IT. 1986. Principal component analysis. New York: Springer-Verlag. 271 p.

Katan LL. 1996. Migration from food contact materials. London: Chapman & Hall. 303 p.

Knapp RB. 1998. Mahalanobis metric. http://www.engr.sjsu.edu/~knapp/HCIRODPR/PR_Mahal/M_metric.htm. San Jose State University. Posted July 16, 1998.

Lawley DN, Maxwell AE. 1971. Factor analysis as a statistical method. New York: American Elsevier Pub. Co. 153 p.

Long RP. 1973. Reference encyclopedia of package printing techniques & equipment. Philadelphia: North American. 295 p.

Marcus L. 2001. Mahalanobis Distance http://www.qc.edu/Biology/fac_stf/marcus/multisyl/fourth.htm. Queens College. Posted August 3, 2001.

Metcalfe DD, Sampson HA, Simon RA. 1997. Food allergy: adverse reactions to foods and food additives. Cambridge, Mass: Blackwell Science. 583 p.

Mielle P. 1996. 'Electronic noses': towards the objective instrumental characterization of food aroma. Trends in Food Sci & Technol 7(12):432-438.

Mielle P, Marquie F. 1998. 'Electronic nose': improvement of the reliability of the product database using new dimensions. Sem in Food Anal 3:93-105.

Nakamoto T, Moriizumi T. 1999. Developments and trends in QCM odor sensing systems. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 123-130.

Nerin C, Cacho J, Gancedo P. 1993. Plasticizers from printing inks in a selection of food packagings and their migration to food. Food Additives and Contaminants 10(4):453-460.

Newman DJ, Luzuriaga DA, Balaban MO. 1999. Odor and Microbiological Evaluation of raw tuna: correlation of sensory and electronic nose data. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 170-184.

Ozdemir M, Ozen BF, Floros JD. 1999. Safety implications from the migration of packaging components into foods. In Proceeding of the 6th Conference of Food Engineering (Barbosa-Canovas GV, and Lombardo SP, editors) – Am Inst of Chem Eng 449-455.

Page BD. 1988. An overview of analytical methods for phthalate esters in foods. In Food and Packaging interactions, JH Hotchkiss, editor. ACS Symposium Series # 365, American Chemical Society, Washington, DC chapter 10.

Page BD, Lacroix GM. 1992. Studies into the transfer and migration of phthalate esters from aluminium foil-paper laminates to butter and margarine. Food Add Contam 9(3): 197-212.

Payne JS. 1998. Electronic nose technology: an overview of current technology and commercial availability. Food Sci and Technol Today 12(4): 196-200.

Pope K. 1995. Technology improves on the nose as scientists try to mimic smell. Wall Street J March 1:B1.

Perkin-Elmer Corporation. 1999. Operators manual for the chemosensory-system QMB6 / HS40XL. Norwalk, CT. HKR Sensorsysteme GmbH.

Persaud KC, Bailey RA, Pisanelli AM, Byun HG, Lee DH, Payne JS. 1999. Conducting polymer sensor arrays. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 318-328.

Robertson G. 1993. Food packaging: principles and practice. New York: Marcel Dekker, Inc. 487 p.

Roussel S, Forsberg G, Steinmetz V, Grenier P, Bellon-Maurel V. 1998. Optimization of electronic nose measurements. Part I: Methodology of output feature selection. J Food Eng 37:207-222.

Roussel S, Forsberg G, Grenier P, Bellon-Maurel V. 1999. Optimization of electronic nose measurements. Part II: Influence of experimental parameters. J Food Eng 39:9-15.

SAS System Help. 1988. SAS Software Version 7. SAS Institute Inc., Cary, NC, USA.

Schaak RE, Dahlberg DB, Miller KB. 1999. The electronic nose: studies on the fundamental response and discriminative power of metal oxide sensors. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 14-26.

Schaller E, Bosset JO. 1998. 'Electronic noses' and their application to food: a review. Sem in Food Anal 3:119-124.

Selke, SE. 1994. Packaging and the environment. Lancaster, Penn: Technometric. 248 p.

Sharma SK, Mulvaney SJ, Rizvi S. 2000. Packaging of foods. In Chapter 18 of Food process engineering: theory and laboratory experiments. New York: John Wiley & Sons, Inc.

Soroka W. 1995. Fundamentals of packaging technology. Lancaster, Penn: Technometric. P 84-85.

Strandburg G, DeLassus PT, Howell BA. 1991. Thermodynamics of permeation of flavors in polymers. In: Risch S, Hotchkiss J, editors. Food and Packaging Interactions II. Washington, DC: American Chemical Society. P 134-135.

Strassburger KJ. 1996. Electronic nose evaluation in the flavor industry: it really works. Food Testing & Anal ():22-27,37.

Strassburger KJ. 1998. Electronic nose technology in the flavor industry: moving from R&D to the production floor. Sem in Food Anal 3:5-13.

Van Deventer D, Mallikarjunan P. 2000. Optimizing detection levels of solvents used in printing inks on plastic films using a chemosensory system. 2000 ASAE Annual Meeting. Milwaukee, Wisconsin. ASAE.

**Chapter 3**

Journal of Food Science

# OPTIMIZING SYSTEM PARAMETERS OF THREE ELECTRONIC NOSE SYSTEMS FOR THE DETECTION OF RETAINED SOLVENTS ON FOOD PACKAGING FILMS

D. Van Deventer — Graduate Student

P. Mallikarjunan * — Assistant Professor

Biological Systems Engineering, VPI&SU, 200 Seitz Hall, Blacksburg VA 24061-0303

Corresponding Author: Dr. Parameswarakumar Mallikarjunan

200 Seitz Hall, Blacksburg, VA 24061-0303

Ph: 540 231 7937 Fax: 540 231 3199 E-mail: kumar@vt.edu

**Optimization of Chemosensory Systems**

**Food Engineering and Physical Properties**

**ABSTRACT**:

The food industry is interested in determining the applicability of using electronic nose instrumentation for odor analysis of retained solvents on packaging films. Response surface methodology was used to generate 2$^{nd}$ order models of sensor response as a function of system and experimental parameters for three systems. Forty-seven of 50 sensor models generated were found to be significant at an $\alpha$-level of 0.05. Optimum settings were selected for future work that allowed adequate signals to be obtained for the full range of examined retained solvents levels. The results indicate potential for electronic nose instrumentation to be used as a complimentary discriminatory tool in quality control for packaging films.

**Keyword(s)**: electronic nose, retained solvents, response surface analysis, printing inks, polymer films

## INTRODUCTION

Foods packaged with polymer-based materials may develop off-odors and flavor deterioration due to aroma absorption and the transfer of undesirable volatiles from packaging to foods (Hotchkiss, 1997). High levels of retained solvents on packaging used during printing pose both a threat to product quality and flavor.

The electronic nose offers an analysis technique that is complimentary to current quality assurance techniques use sensory analysis, GC, GC-olfactory, and GC-mass spectroscopy. These methods require extensive time and preparatory measures, and expertise in understanding the results. As an objective, rapid analysis technique that is more similar to sensory analysis, the electronic nose could become a complimentary tool in quality assurance if it could be demonstrated to be effective in this application.

The fundamental response of each sensor and the overall discriminatory power of the system are affected by the concentration and nature of the volatiles in an aroma, reaction kinetics, sample preparation, and system and experimental parameters. Roussel and others (1998) in order to overcome difficulties with poor gas selectivity and sensitivity, performed work to develop an efficient testing methodology at optimum parameter settings and subsequently examined the influence of various experimental parameters on sensor measurements in an attempt to quantify them (Roussel and others 1999). Schaak and others (1999) examined the effects of the system parameters; injection volume, incubation time, and incubation temperature, and their effect on sensor response and discriminatory power for the MOS sensor based Alpha M.O.S FOX 3000. Bazzo and others in 1999 performed optimization work for the Alpha M.O.S. FOX 4000 system in analyzing high-density polyethylene packaging that allowed the selection of discriminating sensors as well as appropriate sample throughput conditions for that application.

Nakamoto and Morrizumi (1999) reported that the QMB sensor responses could be predicted using computational chemistry allowing for the ability of optimal sensor selection for target odors. In 1999, Hansen and Wiedemann, performed optimization work for a MOS based system investigating experimental and system parameters to optimize the response range of the sensors and enhance their discriminatory power. This work was performed using a full factorial design and examined four experimental parameters, incubation time, incubation temperature, sample mass, and sample agitation rate. Alternatively, response surface designs may be

generated in order to develop models of the sensor responses without having to perform a full factorial design.

The work reported here is the first stage of a comparative performance analysis of electronic nose based systems in detecting residual solvent taints in food packaging films. The hypothesis is the operating settings can be adjusted to maximize the discriminatory power of each system through the development of sensor response models.

## MATERIALS & METHODS

### *Objective*

The objective of this initial work was to determine a single set of system parameter values for each of three electronic nose systems at which food-packaging films with a full range of retained solvent levels can be tested.

This study is part of a performance analysis of the electronic nose system to be used as a complimentary tool for rapid analysis in conjunction with current instrumentation used in the quality control of packaging films.

### *Electronic Nose System Information*

Three electronic nose systems using different sensor technologies, metal-oxide semiconducting sensors, conducting polymer sensors, and quartz microbalance sensors, were optimized for detecting food packaging taints. Each unit is based upon similar principles of operation. A sample headspace is generated and then passed through a sensor chamber by either pressurizing the headspace with a carrier gas or by drawing the headspace aromas with a pump. The sensor array in the chamber then interacts with the complex aroma and the response of each sensor in the array together form a characteristic recognition pattern from that sample. Statistical analyses such as Principal Component Analysis (PCA) and or Discriminant Factorial Analysis (DFA) are then used to both discriminate among groups of samples or to identify an unknown by comparing its characteristic recognition pattern to a known database. To effectively develop a database, each electronic nose must be trained with samples grouped based on known classifications or values that are correlated to some other analytical means.

The metal oxide semiconducting sensor based system examined was the Alpha M.O.S. Model FOX 3000 (Alpha M.O.S., Toulouse, France). This system has twelve sensors with different metal oxide coatings that vary in sensitivity and selectivity. The interaction of the sensors with compounds in the sample aroma is measured as a function of the change in the

conductivity of the sensor. The maximum change in resistance of each of the sensors was used in the analysis. It is connected to an automatic headspace sampler Model HS50 (Alpha M.O.S., Toulouse, France) and uses 10 mL headspace vials with nitrogen as the carrier gas.

The conducting polymer sensor based system examined was the Cyrano Sciences (Pasadena, CA) handheld Cyranose 320 unit. This system has 32 sensors; each coated with a unique carbon-black polymer film. This system is a hand-held unit and was operated manually using a tripod and a heating block to analyze headspace aromas in 10 mL headspace vials. The heating block used was a Reacti-Therm Heating Module (Pierce Chemical Co., Rockford, IL). For this instrument, the interaction of the sensors with compounds in the sample aroma is also measured as a function of the change in sensor conductivity. The values taken for analysis in this system were the maximum change in resistance divided by the original resistance value. The carrier gas in this case is ambient air. As per the manufacturer's recommendation, the carbon and silica gel filters were not used due to the nature of the laboratory environment and low moisture content of the samples.

The quartz-microbalance based system examined in this preliminary work was the HKR Sensorsystems Model QMB6 (Munich, Germany). The system was connected to an automatic headspace sampler (Model HS-40, Perkin-Elmer LLC, Norwalk, CT) as well as an external heat exchanger and chilling unit. The external heat exchanger and chilling unit were used to overcome temperature control difficulties due to the close proximity of the sensor and sample heating chambers. This electronic nose consists of a series of six unique non-selective sensor elements that are coated with gas chromatographic stationary phases of varying polarities. The interaction of the sensors with the compounds in the sample aroma is measured as a function of the change in oscillating frequency of the sensors. The system uses 21 mL headspace vials and nitrogen as the carrier gas. The sensors oscillate at 10 MHz. The adsorption of volatiles from the sample headspace onto the sensor causes a change in the mass of the sensor that results in a measurable change in its oscillating frequency. The resolution of the sensors is ±1 Hz (Perkin-Elmer QMB6 Operators Manual, 1999).

*Sample Preparation Methodology*

The film samples used in the response surface methodology experiments of this study were from a rotogravure printed two-layer film and represented the lower bound of the range of retained solvent levels. The film was reverse printed onto a layer of oriented polypropylene and

then laminated onto a layer of metallized-oriented polypropylene with solvent-based adhesive. It was anticipated that in using electronic nose instrumentation for this packaging application, the most difficult obstacle of the initial phase would be establishing an adequate signal for the 'conforming' samples with low retained solvent levels. Consequently, the response surface methodology was used for optimization of each system using these samples. Samples with the highest expected retained solvent levels would then be used to verify selected settings to ensure that the full range of samples was covered.

The additional samples used in the verification work were also from a rotogravure printed two-layer film. This film was rotogravure printed with approximately 375% ink coverage onto a layer of oriented polypropylene and then laminated onto a layer of low-density polyethylene using a water-based adhesive.

The volatile compounds of interest were not identified through the use of gas chromatograph analyses due to a binding confidentiality disclosure agreement with the supplying manufacturer. The specific information related cannot be shared, although the nature of the retained compounds that are of concern are alcohols and ketones (Robertson 1993). The retained solvent levels of the samples used in this work were determined through GC analysis using the equipment and procedure of the manufacturer. The film samples used in this study are packaging films used with snack food products.

Each sample vial tested in this work was prepared by cutting a single unit impression of the film sample into 2.5 cm wide strips stacked and folded into the headspace vials. One injection was made from each prepared sample. Each of the response surface methodology experiments for each system was performed in triplicate with the average sensor response being the value used in the response surface analysis. The response surface analysis of the collected data was performed for each sensor in each system using the RS-REG procedure in the statistical software package PC-SAS (SAS Inc., Cary, NC). Appropriate surface plots of the response surfaces for each sensor were generated using spreadsheet software.

Control aromas were tested that included ambient air samples, and unprinted samples of oriented polypropylene and low-density polyethylene in order to show that the predominant source of volatiles in the sample aromas was the printed material.

*Parameter Optimization with Response Surface Methodology*

A Box-Behnken centrally rotatable design with three or four parameters and three levels was used for each system to examine the effects of system parameters on the sensor response levels to ink solvent volatiles from on the plastic films. The principle of utilizing response surface analyses is to develop a mathematical expression that approximates the true relationship between response and parameter factors as closely as possible (Devineni and others 1997) without having to perform a full factorial design of experiments.

The system parameters for each system and their range of values that were examined in this study were selected based on volatile kinetics, and consultation with the system manufacturer. Each experiment in the response surface analyses for each system was performed using samples prepared in triplicate.

For the Alpha MOS FOX 3000 system, a three-factor, three-level design (fifteen experiments) was used to investigate the effects of incubation time, incubation temperature, and injection volume. Table 1 shows the experimental design with coded values and the range values of the examined parameters. For the Cyrano Sciences Cyranose 320 instrument, a four-factor, three-level design (27 experiments) was used to investigate the effects of incubation time, incubation temperature, sensor temperature, and pump speed. Table 2 shows the experimental design with coded values and the range of the examined parameters. For the HKR QMB6 system, a three-factor, three-level design (fifteen experiments) was used to investigate the effects of incubation time, incubation temperature, and sensor temperature. Table 3 shows the experimental design with coded values and the range of the examined parameters.

These ranges were established and particular parameters were selected through consulting the manufacturers, relevant literature, and preliminary trials. It may be useful to note that examining higher sampling temperatures is representative of other analyses currently used and is done to increase the volatization of compounds that migrate through diffusion and not by vapor transport. It is also desired to see the effect of this particular parameter in relation to the effects on sensor response caused by other system parameters. It is already expected that increased incubation temperature will result in higher volatile concentrations in the headspace (Roussel and others 1999).

*Procedure*

Response surfaces were obtained for each of the independent sensors for three electronic nose instruments for samples with low levels of retained solvents. This was because it was anticipated that the greatest difficulty would be obtaining a sufficient sensor response for the low-level aromas. On the basis of these plots, initial settings for targeted system parameters were selected. Samples representative of the full range of expected retained solvent levels were then tested to ensure that the setting selections for the parameters fit the full application. Adjustments to the selected system parameters were made using the plots in order to obtain all sensors responses that fell in predetermined acceptable ranges.

Future work will correlate gas chromatographic analyses of samples at varying levels to determine which sensors contribute to the discriminatory power of the instrument and those sensors that are contributing noise. The final optimum settings will be selected based on what sensors are selected for analysis.

**RESULTS & DISCUSSION**

This optimization research is the first part of a larger project involving a comparative performance analysis of these three electronic nose systems in quality control application for food packaging. The expanded use of electronic nose instrumentation in the food industry has been on a per-application basis. In each instance, the instrument must be tested to determine if it can be a suitable complimentary tool.

In some cases, the electronic nose has sufficient selectivity and sensitivity to provide adequate discriminatory power throughout a wide range of system parameters. Also, there are cases where the electronic nose does not demonstrate sufficient discriminatory power in the application at all, regardless of the system parameter settings. In other cases, such as this packaging application, it is necessary to optimize the system parameters to maximize the discriminatory power of the instrument. It is necessary to select the proper settings at which to operate in order to effectively evaluate the instruments in this application. In this particular application, it is ultimately desired to discriminate among ‘conforming’ samples that have low levels of retained printing solvents, and ‘non-conforming’ samples that have higher levels of printing solvents.

*FOX 3000*

An acceptable range of values for sensor response was established as 0.05 $|\Delta R_{max}| / R_0$ for a lower bound, and 1.00 $|\Delta R_{max}| / R_0$ for an upper bound. The data from the fifteen experiments of the response surface methodology were used to generate coefficients for a $2^{nd}$ order polynomial model. For each of the 12 independent sensors in the system, surface plots of the sensor responses were generated as function of incubation time and incubation temperature for nine levels of the remaining parameter, injection volume. In examining these nine plots for each sensor, it was seen that in all cases for all sensors, the maximum sensor response was achieved with the incubation temperature set to its upper bound of 75 °C. The sensor response values were within the acceptable range. Consequently, the value of 75 °C for the sample incubation temperature was selected.

A single response surface was then plotted for each sensor as a function of incubation time and injection volume with the incubation temperature set to 75 °C. Figure 4 and Figure 5 show the response of sensors 1 and 10, respectively. The shape of the surface generated for sensor 1 is highly representative of the surface plots generated for sensors 1-6. The shape of the surface generated for sensor 10 is highly representative of the surface plots generated for sensors 7-12. It is seen in comparing Figure 4 and Figure 5, that the injection volume parameter has an inverse effect on the sensor responses of sensors 1-6 as compared with sensors 7-12. Increasing the injection volume increases the response of sensors 1-6 and decreases the response of sensors 7-12. It is also seen that the parameter of incubation time also has an inverse effect on the two groups of sensors. Sensors 7-12 increase as the incubation time approaches its lower bound. Sensors 2, 5, and 6 increase as the incubation time is increased, and sensors 1, 3, and 4 increased to a maximum and then decreased.

The coefficient values for each of the system parameter linear terms and whether they were significant with an $\alpha$=0.05 are given in Table 4. It is seen from the table that the overall models obtained were significant for all of the sensors and had $R^2$ values of 0.92 or greater. It is also shown through the model coefficients that the injection volume parameter affects the sensor response in all cases. Although the proportion varies from sensor to sensor, in all cases the magnitude of the injection volume coefficient was the greatest, and the incubation time was least in magnitude.

If the incubation time were shown to have no effect on sensor response, the overall project objective of using the electronic nose instrument as a complimentary tool for rapid odor analysis would dictate that the incubation time be set at its lower bound. Because the incubation time is the least influential parameter in the model for each of the sensors, it was decided to use an incubation time of 5 minutes for the same practical reason. Had this parameter been more influential in the overall model, it may have affected its setting selection.

Depending on the extent to which each group of sensors contributes to the overall discriminatory power of the system, it may be beneficial to reduce the number of sensors than to use all twelve. This will be established in future work. Using a null hypothesis that all twelve sensors contribute to the discriminatory power of the system, a compromise for injection volume between the opposing sensor groups was sought. Projected values for system response were taken from the surface plots and calculated as a percent of the maximum possible value for each sensor. An injection value of 150 μL (coded value of –0.75) achieved an average of a 78% of maximum value for sensors 1-6 and an average of a 76% of maximum value for sensors 7-12. Consequently, an injection volume of 150 μL was the initial selected setting.

It was anticipated it would be more difficult to select adequate system parameter settings to accommodate the low level signals of 'conforming' samples with low levels of retained solvents. The response surface methodology was performed using a conforming sample, and subsequently the parameter settings were selected on the basis of this data. To verify that the selected settings were valid for the full range of retained solvent levels, the samples with the highest level of retained solvents, as measured through gas chromatography analysis, was tested at these settings. The 'non-conforming' samples with the highest retained solvent levels that were examined demonstrated sensor responses that fell within the required range of 0.05 – 1.00 $|\Delta R_{max}| / R_0$.

The selected parameter settings for the AlphaM.O.S. FOX 3000 in this project application include an incubation temperature of 75 °C, an incubation time of 5 minutes, and an injection volume of 150 μL.

*Cyranose 320*

An acceptable range of values for sensor response was established as 0.001 $|\Delta R_{max}| / R_0$ for a lower bound, and 0.500 $|\Delta R_{max}| / R_0$ for an upper bound. For each of the 32 independent sensors in the system, surface plots of the sensor responses were generated as function of

incubation time and incubation temperature for nine levels of the parameter injection volume at each of the three possible levels of pump speed. In examining these 27 plots for each sensor, it was again seen that in all cases for all sensors, the maximum sensor response was achieved with the incubation temperature set to its upper bound of 100 °C. The sensor response values were within the acceptable range. Consequently, this value of 100 °C was initially selected for the sample incubation temperature. In addition, the maximum value for each of the sensors was also achieved with the pump speed parameter set to a setting of 'Low' or 50 cc/min. This is the setting for pump speed.

A single response surface was then plotted for each sensor as a function of incubation time and injection volume with the incubation temperature set to 100 °C and the pump speed set to 'Low' or 50 cc/min. Figure 6 and Figure 7 show the response of sensors 10 and 22, respectively. The shape of the surface generated for sensor 22 (Figure 7) is highly representative of the surface plots generated for all of the sensors 1-32 with the exception of sensor 10. Sensor 22 was chosen for Figure 7 to be representative of the 31 similar sensors because it demonstrated the weakest signal response. Therefore, settings that result in an adequate signal for sensor 22 would also result in an adequate minimum signal for all of the 31 similar sensors. In examining the surface plot in Figure 7, it is seen that as the incubation time increased and the sensor temperature decreased, the sensor response increased. Sensor 10 demonstrates to be the exception in the system (Figure 6) as its sensor response has a saddle point and the maximum sensor response is also achieved with the maximum sensor temperature of 50 °C. As the sensor temperature increased from 40 °C to 50 °C, the response of sensor 10 decreased and then increased after the sample temperature was greater than 44 °C.

The coefficient values for each of the system parameter linear terms and whether they were significant with an $\alpha$=0.05 are given in Table 5. It is seen from the table that the overall models obtained were significant for all of the sensors and had $R^2$ values of 0.91 or greater. It is also shown through the model coefficients that the incubation temperature is the parameter that most affects the sensor response in all cases. It was also found to be significant at $\alpha$=0.05 for all of the sensors. Although the proportions vary from sensor to sensor, in ranking the model coefficients it is seen that the incubation temperature contributes the most followed by the sensor temperature. With few exceptions, the magnitude of the incubation time coefficient was greater than that of the pump speed. For four of the sensors, the incubation time was found not to be

significant and for fourteen of the sensors, the pump speed was not found to be significant. For two of the sensors, the sensor temperature coefficient was not found to be significant in the overall model.

From a practical perspective, as long as the incubation temperature is set to 100 °C, the system maintains a sufficient throughout the full range of the remaining parameters. This allows the incubation time to be set to the lower bound value of 5 minutes in order to obtain a more rapid analysis. The value to be initially selected for sample temperature is 40 °C. This value produces the greatest signal for 31 of the 32 sensors and an adequate signal for the remaining sensor.

It is possible that some of the sensors are primarily detecting compounds that are not of interest in this application, such as water vapor. In such cases, these sensors could be contributing noise to the system and reducing its overall discriminatory power. This will be established in a future work, at which time it may be beneficial to reduce the number of sensors used for analysis from the original 32.

To verify that the selected settings were valid for the full range of retained solvent levels, the samples with the highest level of retained solvents were also tested at these settings. The 'non-conforming' samples with the highest retained solvent levels that were examined demonstrated sensor responses that fell well within the required range of 0.001 – 0.500 $|\Delta Rmax| / R_0$ as the maximum obtained response was 0.22 $|\Delta Rmax| / R_0$.

The selected parameter settings for the Cyrano Sciences Cyranose 320 in this project application include a incubation temperature of 100 °C, a incubation time of 5 minutes, a sample temperature of 40 °C, and a pump speed of 50 cc/min or 'Low' setting.

*QMB6*

Prior to the study, it was determined from the specifications of the manufacturer that if the response value for any of the sensors were less than 20 Hz, this equipment would be deemed unacceptable for use in this application. The maximum acceptable frequency change would be 5000 Hz.

In examining the nine surface plots for each sensor, it was again seen that in all cases for all sensors, the maximum sensor response was achieved with the incubation temperature set to its upper bound of 100 °C. It was not a concern to heat the sample above ambient temperature as the gas chromatography method used in industry incubates the sample at elevated temperatures.

A single response surface was then plotted for each sensor as a function incubation time and sample temperature with the incubation temperature set to 100 °C. The response surfaces for sensors 1-6 are shown in Figures 8-13, respectively. The response surface for each sensor is given separately in this case because they are all unique, and in each case the axes are rotated to obtain a suitable isometric view for that plot. The coefficient values for each of the system parameter linear terms and whether they were significant with an $\alpha$=0.05 are given in Table 6.

Most notably, it is seen from the table that the overall 2nd order polynomial models that were obtained were not significant for all of the sensors in this case. The models for sensors 3, 5, and 6 were significant and had $R^2$ values of 0.95, 0.94, 0.96. The $R^2$ values were 0.83, 0.82, and 0.79 for the models that were built for sensors 1, 2, and 4. However, it should be noted that for sensors 1, 2 and 4 the surface plots were generated using models that were not found to be significant and so it cannot be conclusively stated that the surface plots from these two models accurately project the corresponding sensor response for sensors 1, 2 and 4 at an $\alpha$-level of 0.05. These plots would only be able to be considered significant if the $\alpha$-level were initially chosen at 0.20 or higher. Therefore, it is very important to verify the performance of these sensors at settings selected using data from any of these models. In examining the original nine plots generated for each sensor and verified by the magnitude of the linear coefficients in Table 6, it was seen that with the exception of sensor 4, the incubation temperature was the parameter that most affected the overall sensor response. For sensor 4, the parameter making the greatest contribution was found to be the sensor temperature. For sensors 1, 2, and 3, it is seen from the surface plots that the least contributing parameter is the sensor temperature, and for sensors 4, 5, and 6, it is shown in the surface plots that the incubation time is the least contributing parameter.

In any 2nd order polynomial model, the quadratic and cross product terms contribute to the shape of the surface plot generated. In this study, it was seen that in each of the three systems, the coefficients for 2nd order terms and cross products were predominantly found not to be significant at $\alpha$-level of 0.05 and were also generally of a lower order of magnitude than the linear terms. Consequently, they are not presented here, as they do not provide useful information. Ultimately, full effect of each parameter on the model is shown in the generated surface plots. In performing the response surface methodology experiments, it was necessary to install an external heat exchanger and chilling unit to more effectively control the environment.

It was seen universally for the QMB6 system, that the greatest sensor response was achieved at a sensor temperature of 40 °C, and with the exception of sensor 4 again, it was also achieved at the highest level for incubation time of 25 minutes. Because it can be compensated for through adjustments of the other parameters, an initial incubation time of 5 minutes was again chosen. In addition, the sensor temperature was initially set to 40 °C to maximize the signal of the samples with the lower levels of retained solvents.

Upon verifying the initially selected settings of a incubation temperature of 100 °C, a incubation time of 5 minutes, and a sensor temperature of 40 °C, with samples representing the minimum and maximum expected retained solvent levels, problems were encountered and the usefulness of the generated surface plots was demonstrated. The major problem that occurred was that the 'non-conforming' samples which had approximately three times greater retained solvent levels than those of the 'conforming' low retained solvent levels, caused an overload on sensor 3. Damage to the sensor was suspected as the readings were well above the stated acceptable range of 20-5000 Hz. A heptane standard was tested to check if the sensor had been damaged, but the results indicated that the sensor had fully recovered. The heptane was tested and matched with other heptane samples tested before any problems were suspected with the sensor.

Coincident with this problem, it also became evident that it would be necessary to change the sampling method if future work was to include film samples from an assorted range of products. This is primarily due to the thickness of low-density polyethylene films. The use of unit impressions in sampling had been initially chosen to aid in introducing representative samples to the electronic nose from multiple lots of a film product. For oriented-polypropylene films, due to its relatively thin thickness, a wide range of surface areas can be sampled, and this method proved to be effective. However, for any film containing low-density polypropylene, it was not feasible to use a 10 or 21 mL headspace vial to sample film impressions with a surface area greater than a section approximately 193.5 $cm^2$ (30.0 $in^2$) in area. In order to establish a universal sampling method that would allow objective analyses of a full assortment of film polymers, a set surface area to be taken from each sample was established. With the new method, a 51.6 $cm^2$ (8.0 $in^2$) section that covers the widest range of printing colors is selected and recorded for each film product. The specific 51.6 $cm^2$ (8.0 $in^2$) sections taken from each film sample were recorded and used every time that product's film impressions were sampled. These

adjustments to the sampling method were made through consulting members of the food industry doing similar work.

For the particular film product that was used to perform the response surface analyses, this sampling method change resulted in a reduction of about 75% in surface. Upon testing the full range of samples with this new method, it was seen that sensor 3 was still overloaded while the responses of the other sensors decreased. The two other electronic nose systems previously discussed were also re-examined to verify if the selected parameters still provided sensor signals within the appropriate range. Both of the systems demonstrated lower sensor responses as expected, however, the signals all fell within the adequate range.

Adjustments to the sampling parameters were still needed to bring sensor 3 of the QMB6 system back into its acceptable response range. The surface plot for sensor 3 shown in Figure 10, shows that increasing the sensor temperature would reduce the sensor response. It was desired to first adjust this parameter. This was due to the desire to keep as many of the system parameters consistent from one system to the next in the subsequent comparative performance analyses. The high and low level samples were tested while increasing the sensor temperature. It was found that at a sample temperature of 60 °C, some of the replications for the high level samples began to cause a response in sensor 3 that was within the acceptable range. If the sample temperature was increased to 75 °C, nearly all of the replications were within the acceptable range. At a sample temperature of 80 °C, all of the high level samples were within the acceptable range. After each overload of sensor 3, the heptane standard was used to check that its condition had not deteriorated. For sensors 2 and 5, the low level film samples caused sensor responses that were below the lower bound value of 20 Hz set through discussion with the manufacturer. However, the standard deviation of 20 replications was found to be 0.9 and 0.6 Hz, consequently, the reproducibility was found to be sufficient.

As a result, for the HKR Sensorsystems QMB6 unit, the settings chosen for future work included an incubation temperature of 100 °C, an incubation time of 5 minutes, and a sensor temperature of 80 °C.

It should be addressed here that control samples were also run in all systems to affirm the theory that the compounds dominating the sample aromas are from the printing compounds. The volatiles analyzed by the electronic nose instruments in this study may be from compounds in the inks, compounds in the air, or compounds from the plastic films themselves. To address the

question of whether the majority of the volatiles were in fact coming from the ink solvents and not perhaps from plastic films themselves, control samples that consisted of samples of air, unprinted OPP, and unprinted LDPE were analyzed at the selected settings for each system. The samples of unprinted polymers had a greater response than the air only indicating that they contribute something to the signal of the printed films. However, the magnitude of the sensor responses was minute in comparison to the printed film samples showing that the signal responses of the targeted samples were in fact dominated by the volatiles present from the printing inks and solvents.

In examining the surface plots for the array of sensors, it can be seen that the conducting polymer based system is the most robust in terms of the range of settings at which it has adequate sensitivity for this application. The selectivity of the systems can only be assessed through future work discriminating between extensive databases of 'conforming' and 'non-conforming' films. The quartz microbalance based system demonstrated the least robust system in terms of the range of settings at which all of sensors can achieve an adequate level of sensitivity.

It may not have been absolutely necessary to perform the model development for each sensor, and setting selection could very possibly have been accomplished using only theory based on sensor coating reactivity and trial-and-error experimentation. However, this was an attempt to add more quantitative and scientific data to the selection process and justification for selected settings and future adjustments. The usefulness of response surface methodology in the optimization of electronic nose instrumentation was seen from the results of this study, and a full factorial design to obtain sensor response models was avoided.

The quantification of the relative effects of each parameter is very useful. It allows practical decisions to be made and justified because their relative effects on sensor response are known. Reduced performance through one parameter setting can be compensated for through the adjustment of another. The user can set the priority of the parameters however it is relevant to an application when making adjustments. In this application, the sensor response in all cases increased as the thermostatting temperature of the sample was increased. This was expected. However, thermostatting temperature was also found in most cases to be the most significant parameter affecting the sensor response in this application. As a result, it may be concluded that if major adjustments are needed to obtain a desired range of sensor responses, thermostatting temperature is the primary parameter to make adjustments with.

It is possible that some of the sensors in each system are primarily detecting compounds that are not of interest in this application, such as water vapor. In such cases, these sensors could be contributing noise to the system and reducing its overall discriminatory power of the PCA analyses used by each system to achieve separation among identified samples. This will be established in future work, at which time it may be beneficial to reduce the number of sensors used for analysis from the original number available in the array. This will be accomplished through data correlation to gas chromatography analyses.

The data presented here is the first step in a project which will involve the development of databases of characteristic recognition patterns for each of the different packaging films with 'conforming' and 'non-conforming' levels of volatiles present after printing, and test the performance of the equipment in its ability to discriminate between these different classes of films.

**CONCLUSION**

Models built using response surface methodology can be used to aid in making adjustments to the sensor array response to optimize an electronic nose system for a particular application. At the above stated settings for each system, adequate signals can be obtained for the full range of levels of retained solvents on food packaging films that are being examined. This indicates that there is potential for electronic nose instrumentation to show discrimination between films with 'conforming' and 'non-conforming' retained solvent levels and be used as a complimentary analysis tool in quality control of food packaging.

**REFERENCES**

Bazzo S, Loubet F, Labreche S, and Tan TT. 1999. Optimization of Fox sensor array system for QC packaging in factory environment. Robustness, sample throughput and transferability. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 225-144.

Devineni N, Mallikarjunan P, Chinnan MS, Phillips RD. 1997. Supercritical fluid extraction of lipids from deep-fried food products. J Amer Oil Chem Soc 74(12):1517-1523.

Hansen WG, Wiedemann SC. 1999. Evaluation and optimization of an electronic nose. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 131-144.

Hotchkiss JH. 1997. Food-packaging interactions influencing quality and safety. Food Additives and Contaminants 14(6):601-607.

Nakamoto T, Moriizumi T. 1999. Developments and trends in QCM odor sensing systems. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 123-130.

Ozdemir M, Ozen BF, Floros JD. 1999. Safety implications from the migration of packaging components into foods. In Proceeding of the 6th Conference of Food Engineering (Barbosa-Canovas GV, and Lombardo SP, editors) – Am Inst of Chem Eng 449-455.

Perkin-Elmer Corporation. 1999. Operators manual for the chemosensory-system QMB6 / HS40XL. Norwalk, CT. HKR Sensorsystems GmbH.

Robertson G. 1993. Food packaging: principles and practice. New York: Marcel Dekker, Inc. 487 p.

Roussel S, Forsberg G, Steinmetz V, Grenier P, Bellon-Maurel V. 1998. Optimization of electronic nose measurements. Part I: Methodology of output feature selection. J Food Eng 37:207-222.

Roussel S, Forsberg G, Grenier P, Bellon-Maurel V. 1999. Optimization of electronic nose measurements. Part II: Influence of experimental parameters. J Food Eng 39:9-15.

Schaak RE, Dahlberg DB, Miller KB. 1999. The electronic nose: studies on the fundamental response and discriminative power of metal oxide sensors. In: Hurst J, editor. Electronic noses & sensor array based systems: design & applications. Lancaster, Penn: Technometric. P 14-26.

Table 1. Experimental design of response surface analysis experiments for the Alpha M.O.S. FOX 3000 using coded value parameters in a Box-Behnken centrally rotatable design with three factors and three levels.

| Experiment No. | Incubation Time min | Incubation Temperature °C | Injection Volume µL |
|---|---|---|---|
| 1 | (15) 1 | (75) 1 | (300) 0 |
| 2 | (15) 1 | (45) -1 | (300) 0 |
| 3 | (5) -1 | (75) 1 | (300) 0 |
| 4 | (5) -1 | (45) -1 | (300) 0 |
| 5 | (10) 0 | (60) 0 | (300) 0 |
| 6 | (15) 1 | (60) 0 | (500) 1 |
| 7 | (15) 1 | (60) 0 | (100) -1 |
| 8 | (5) -1 | (60) 0 | (500) 1 |
| 9 | (5) -1 | (60) 0 | (100) -1 |
| 10 | (10) 0 | (60) 0 | (300) 0 |
| 11 | (10) 0 | (75) 1 | (500) 1 |
| 12 | (10) 0 | (75) 1 | (100) -1 |
| 13 | (10) 0 | (45) -1 | (500) 1 |
| 14 | (10) 0 | (45) -1 | (100) -1 |
| 15 | (10) 0 | (60) 0 | (300) 0 |

Table 2. Experimental design of response surface analysis experiments for the Cyrano Sciences Cyranose 320 using coded value parameters in a Box-Behnken centrally rotatable design with four factors and three levels.

| Experiment No. | Incubation Time min | Incubation Temperature °C | Sensor Temperature °C | Pump Speed cc / min |
|---|---|---|---|---|
| 1 | (25) 1 | (70) 0 | (45) 0 | (180 High) 1 |
| 2 | (25) 1 | (70) 0 | (45) 0 | (50 Low) -1 |
| 3 | (5) -1 | (70) 0 | (45) 0 | (180 High) 1 |
| 4 | (5) -1 | (70) 0 | (45) 0 | (50 Low) -1 |
| 5 | (10) 0 | (100) 1 | (50) 1 | (120 Med) 0 |
| 6 | (10) 0 | (100) 1 | (40) -1 | (120 Med) 0 |
| 7 | (10) 0 | (40) –1 | (50) 1 | (120 Med) 0 |
| 8 | (10) 0 | (40) –1 | (40) -1 | (120 Med) 0 |
| 9 | (10) 0 | (70) 0 | (45) 0 | (120 Med) 0 |
| 10 | (25) 1 | (70) 0 | (50) 1 | (120 Med) 0 |
| 11 | (25) 1 | (70) 0 | (40) -1 | (120 Med) 0 |
| 12 | (5) -1 | (70) 0 | (50) 1 | (120 Med) 0 |
| 13 | (5) -1 | (70) 0 | (40) -1 | (120 Med) 0 |
| 14 | (10) 0 | (100) 1 | (45) 0 | (180 High) 1 |
| 15 | (10) 0 | (100) 1 | (45) 0 | (50 Low) -1 |
| 16 | (10) 0 | (40) -1 | (45) 0 | (180 High) 1 |
| 17 | (10) 0 | (40) -1 | (45) 0 | (50 Low) -1 |
| 18 | (10) 0 | (70) 0 | (45) 0 | (120 Med) 0 |
| 19 | (25) 1 | (100) 1 | (45) 0 | (120 Med) 0 |
| 20 | (25) 1 | (40) -1 | (45) 0 | (120 Med) 0 |
| 21 | (5) -1 | (100) 1 | (45) 0 | (120 Med) 0 |
| 22 | (5) -1 | (40) -1 | (45) 0 | (120 Med) 0 |
| 23 | (10) 0 | (70) 0 | (50) 1 | (180 High) 1 |
| 24 | (10) 0 | (70) 0 | (50) 1 | (50 Low) -1 |
| 25 | (10) 0 | (70) 0 | (40) -1 | (180 High) 1 |
| 26 | (10) 0 | (70) 0 | (40) -1 | (50 Low) -1 |
| 27 | (15) 0 | (70) 0 | (45) 0 | (120 Med) 0 |

Table 3. Experimental design of response surface analysis experiments for the HKR Sensorsystems QMB6 using coded value parameters in a Box-Behnken centrally rotatable design with three factors and three levels.

| Experiment # | Incubation Time min | Incubation Temperature °C | Sensor Temperature °C |
|---|---|---|---|
| 1 | (15) 1 | (100) 1 | (60) 0 |
| 2 | (15) 1 | (40) –1 | (60) 0 |
| 3 | (5) –1 | (100) 1 | (60) 0 |
| 4 | (5) –1 | (40) –1 | (60) 0 |
| 5 | (10) 0 | (70) 0 | (60) 0 |
| 6 | (15) 1 | (70) 0 | (80) 1 |
| 7 | (15) 1 | (70) 0 | (40) –1 |
| 8 | (5) –1 | (70) 0 | (80) 1 |
| 9 | (5) –1 | (70) 0 | (40) –1 |
| 10 | (10) 0 | (70) 0 | (60) 0 |
| 11 | (10) 0 | (100) 1 | (80) 1 |
| 12 | (10) 0 | (100) 1 | (40) –1 |
| 13 | (10) 0 | (40) –1 | (80) 1 |
| 14 | (10) 0 | (40) –1 | (40) –1 |
| 15 | (10) 0 | (70) 0 | (60) 0 |

Table 4. Coefficients of the linear terms from the 2nd Order polynomial models for the Alpha MOS FOX 3000 sensors obtained from the response surface methodology experiments.

| Model | $R^2$ | Intercept | Incubation Time | Incubation Temperature | Injection Volume |
|---|---|---|---|---|---|
| Sensor1 | 0.9208 | 2.49 | 0.02* | 0.01* | 0.10 |
| Sensor2 | 0.9957 | 466.64 | 6.18 | 14.94 | 64.63 |
| Sensor3 | 0.9946 | 437.82 | 4.57 | 11.46 | 49.89 |
| Sensor4 | 0.9910 | 224.30 | 1.74* | 4.86 | 21.85 |
| Sensor5 | 0.9968 | 259.55 | 2.62 | 6.74 | 30.83 |
| Sensor6 | 0.9983 | 46.42 | 1.01 | 2.11 | 8.68 |
| Sensor7 | 0.9989 | 68.20 | -4.73 | -9.68 | -47.28 |
| Sensor8 | 0.9997 | 29.12 | -1.46 | -2.81 | -13.74 |
| Sensor9 | 0.9998 | 57.55 | -1.36 | -2.50 | -11.61 |
| Sensor10 | 0.9996 | 29.25 | -1.64 | -3.16 | -15.70 |
| Sensor11 | 0.9988 | 58.30 | -4.24 | -8.62 | -42.80 |
| Sensor12 | 0.9985 | 33.74 | -2.61 | -5.30 | -26.48 |

* - Value not found to be significant ($\alpha$=0.05)

Table 5. Coefficients of the linear terms from the 2nd Order polynomial models for the Cyrano Sciences Cyranose 320 sensors obtained from the response surface experiments.

| Model | $R^2$ | Intercept | Incubation Time | Incubation Temperature | Sensor Temperature | Pump Speed |
|---|---|---|---|---|---|---|
| Sensor1 | 0.9894 | 0.004817 | 0.000647 | 0.004565 | -0.001090 | -0.000378 |
| Sensor2 | 0.9890 | 0.005057 | 0.000646 | 0.004716 | -0.001130 | -0.000319* |
| Sensor3 | 0.9895 | 0.006790 | 0.000926 | 0.006359 | -0.001490 | -0.000461 |
| Sensor4 | 0.9861 | 0.005353 | 0.000674 | 0.004921 | -0.001290 | -0.000316* |
| Sensor5 | 0.9701 | 0.029360 | 0.004491 | 0.031616 | -0.010830 | -0.004598 |
| Sensor6 | 0.9516 | 0.024740 | 0.010785 | 0.053238 | -0.020330 | -0.008164* |
| Sensor7 | 0.9840 | 0.003327 | 0.000281 | 0.002092 | -0.000500 | -0.000348 |
| Sensor8 | 0.9900 | 0.002863 | 0.000323 | 0.002518 | -0.000570 | -0.000153* |
| Sensor9 | 0.9897 | 0.016257 | 0.002211 | 0.015398 | -0.002800 | -0.000894* |
| Sensor10 | 0.9662 | 0.003773 | 0.000331 | 0.002616 | -0.000134* | -0.000418 |
| Sensor11 | 0.9833 | 0.004430 | 0.000492 | 0.003656 | -0.001020 | -0.000314* |
| Sensor12 | 0.9925 | 0.008423 | 0.001075 | 0.007187 | -0.000840 | -0.000485 |
| Sensor13 | 0.9780 | 0.003533 | 0.000324 | 0.002529 | -0.000760 | -0.000290 |
| Sensor14 | 0.9884 | 0.004247 | 0.000423 | 0.002849 | -0.000640 | -0.000308 |
| Sensor15 | 0.9861 | 0.007003 | 0.000749 | 0.005224 | -0.001270 | -0.000480 |
| Sensor16 | 0.9834 | 0.004443 | 0.000364 | 0.002611 | -0.000650 | -0.000357 |
| Sensor17 | 0.9798 | 0.004417 | 0.000338 | 0.002843 | -0.000520 | -0.000545 |
| Sensor18 | 0.9893 | 0.008093 | 0.001030 | 0.006653 | -0.001500 | -0.000276* |
| Sensor19 | 0.9901 | 0.004267 | 0.000512 | 0.003481 | -0.000710 | -0.000119* |
| Sensor20 | 0.9909 | 0.011287 | 0.001557 | 0.009953 | -0.001880 | -0.000372* |
| Sensor21 | 0.9825 | 0.002677 | 0.000224 | 0.001613 | -0.000430 | -0.000176 |
| Sensor22 | 0.9706 | 0.002630 | 0.000191* | 0.000199 | -0.000340 | -0.000226* |
| Sensor23 | 0.9705 | 0.014783 | 0.001301* | 0.011923 | -0.004170 | -0.001894 |
| Sensor24 | 0.9076 | 0.001233 | 0.000160* | 0.001233 | -0.000280* | -0.000141* |
| Sensor25 | 0.9852 | 0.004780 | 0.000452 | 0.003153 | -0.000870 | -0.000277 |
| Sensor26 | 0.9781 | 0.010393 | 0.001314 | 0.010325 | -0.002850 | -0.000923* |
| Sensor27 | 0.9894 | 0.005290 | 0.000527 | 0.003843 | -0.000850 | -0.000378 |
| Sensor28 | 0.9887 | 0.018467 | 0.002916 | 0.019501 | -0.003080 | -0.000808* |
| Sensor29 | 0.9903 | 0.018050 | 0.002423 | 0.017936 | -0.002890 | -0.001159* |
| Sensor30 | 0.9840 | 0.004153 | 0.000378 | 0.003048 | -0.000610 | -0.000401 |
| Sensor31 | 0.9550 | 0.012630 | 0.001589* | 0.014947 | -0.005100 | -0.002373 |
| Sensor32 | 0.9885 | 0.004483 | 0.000428 | 0.003264 | -0.000690 | -0.000328 |

* - Value not found to be significant ($\alpha$=0.05)

Table 6. Coefficients of the linear terms from the 2nd Order polynomial models for the HKR Sensorsystems QMB6 sensors obtained from the response surface methodology experiments.

| Model | $R^2$ | Intercept | Incubation Time | Incubation Temperature | Sensor Temperature |
|---|---|---|---|---|---|
| Sensor1 | 0.8324* | 5.233* | 2.838* | 12.438 | -0.900 |
| Sensor2 | 0.8192* | 9.167* | 4.550* | 13.413 | -3.538 |
| Sensor3 | 0.9500 | 103.533 | 5.900* | 18.250 | 10.867 |
| Sensor4 | 0.7921* | -1.567* | -2.463* | 21.300* | -24.613 |
| Sensor5 | 0.9419 | 2.533* | 2.400* | 15.675 | -11.275 |
| Sensor6 | 0.9647 | 16.533 | 1.300* | 16.538 | -9.563 |

* - Value not found to be significant ($\alpha$=0.05)

FIGURE CAPTIONS

Figure 1. AlphaM.O.S. FOX 3000 workstation. 1) AlphaM.O.S. FOX 3000, 2) HS-50 automated headspace sampler, 3) Nitrogen carrier gas, 4) Controlling computer.

Figure 2. Cyrano Sciences Cyranose 320 workstation. 1) Cyranose 320, 2) Sample heating block, 3) Controlling computer.

Figure 3. HKR Sensorsystems QMB6 workstation. 1) QMB6 Sensor Chamber, 2) HS40 automated headspace sampler, 3) External heat exchanger, 4) External chilling unit, 5) Nitrogen carrier gas, 6) Controlling computer.

Figure 4. Response surface model for sensor 1 of 12 for the AlphaM.O.S. FOX 3000.

Figure 5. Response surface model for sensor 10 of 12 for the AlphaM.O.S. FOX 3000.

Figure 6. Response surface model for sensor 10 of 32 for the Cyranose 320.

Figure 7. Response surface model for sensor 22 of 32 for the Cyranose 320.

Figure 8. Response surface model for sensor 1 of 6 for the QMB6.

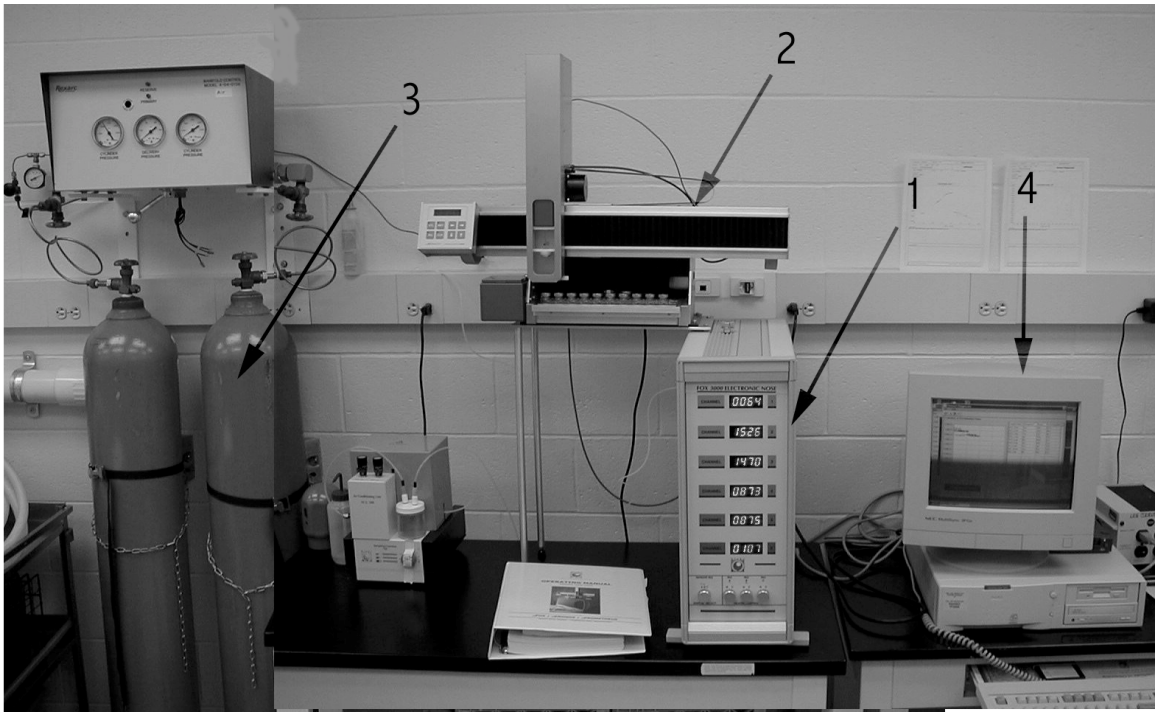
Figure 9. Response surface model for sensor 2 of 6 for the QMB6.

Figure 10. Response surface model for sensor 3 of 6 for the QMB6.

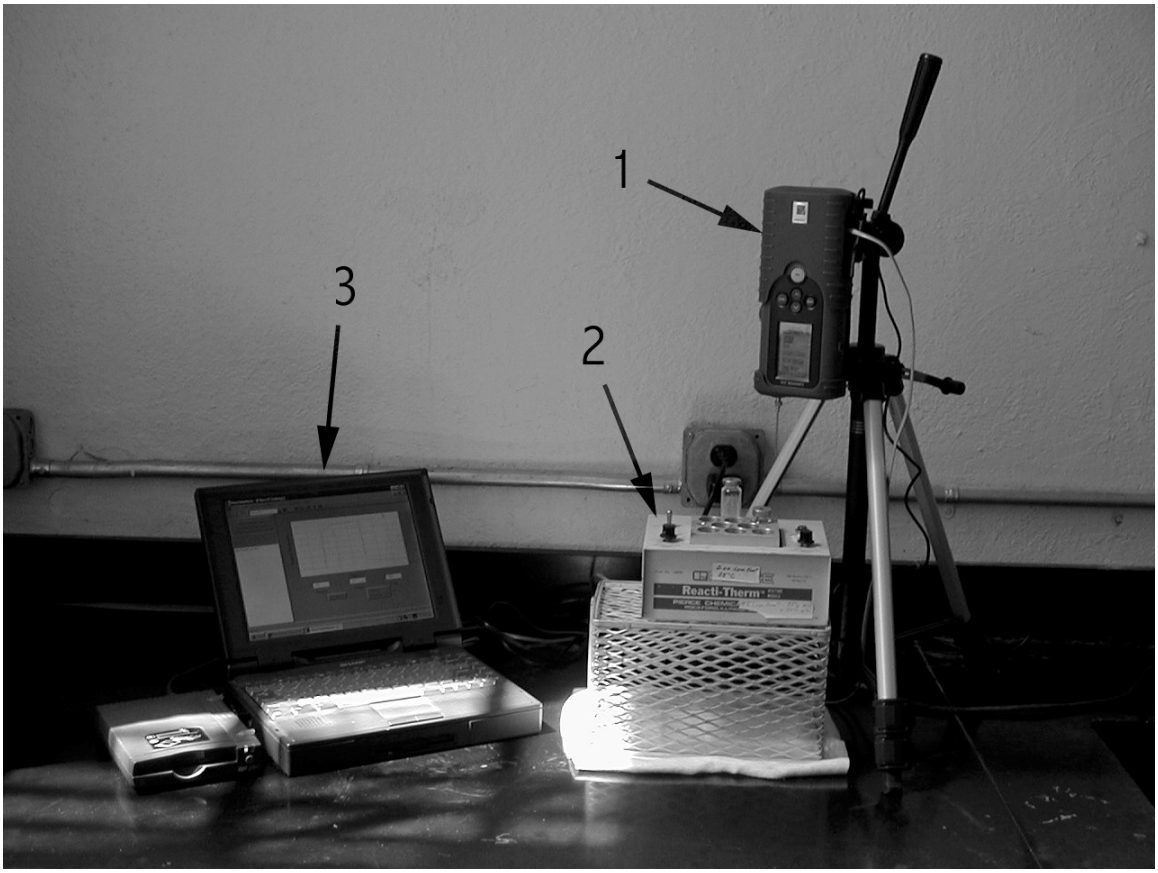
Figure 11. Response surface model for sensor 4 of 6 for the QMB6.

Figure 12. Response surface model for sensor 5 of 6 for the QMB6.

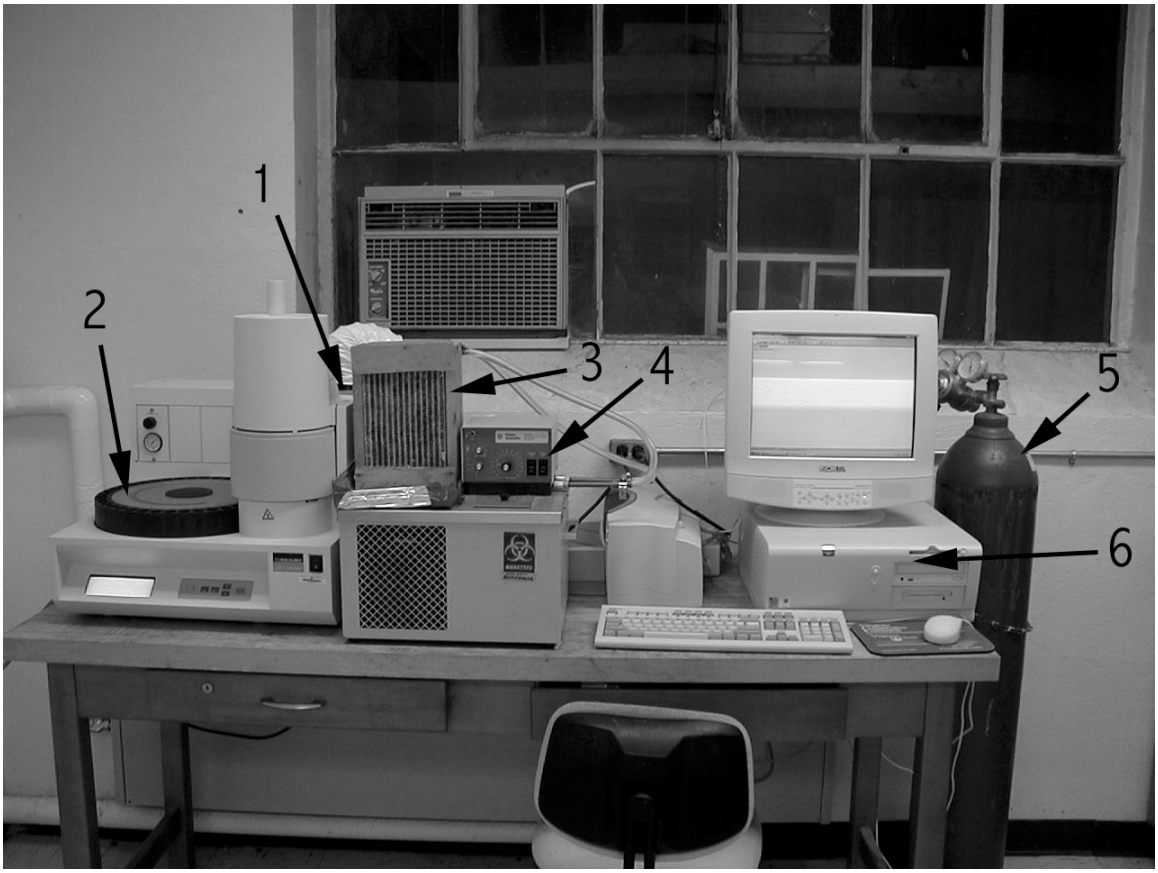
Figure 13. Response surface model for sensor 6 of 6 for the QMB6.



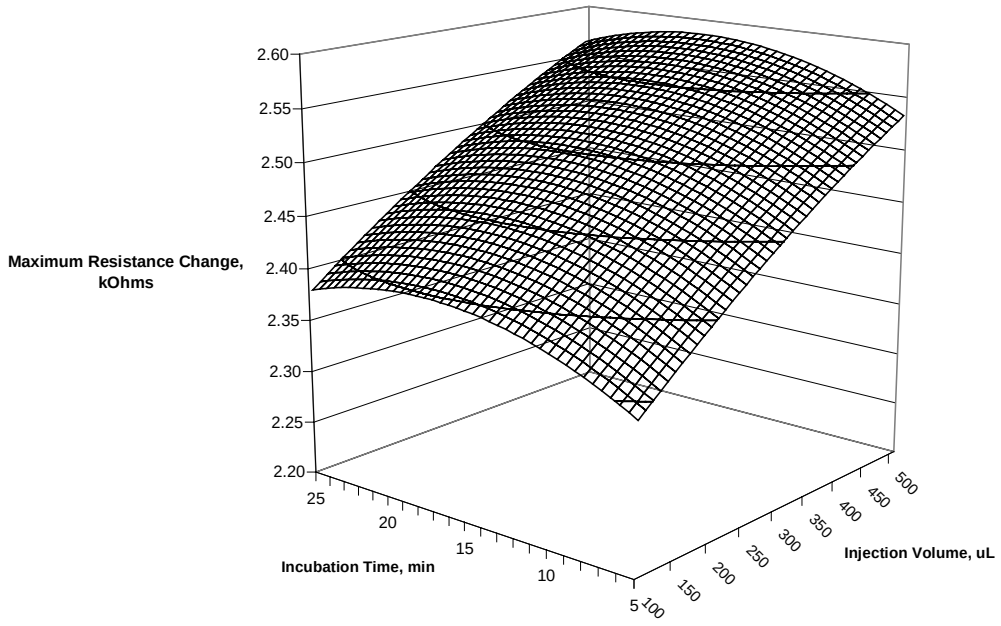

1




2

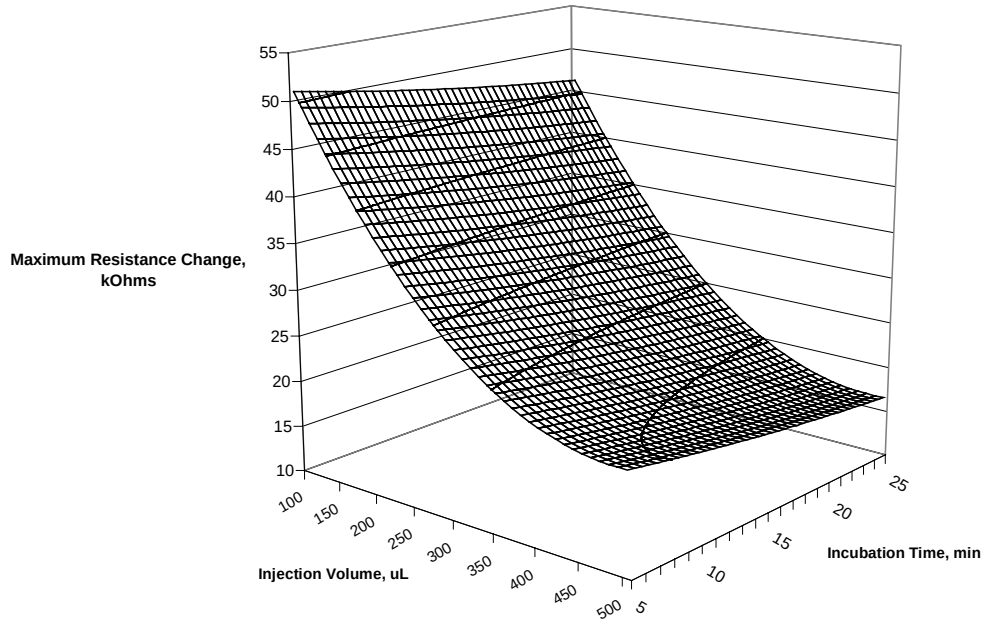



3



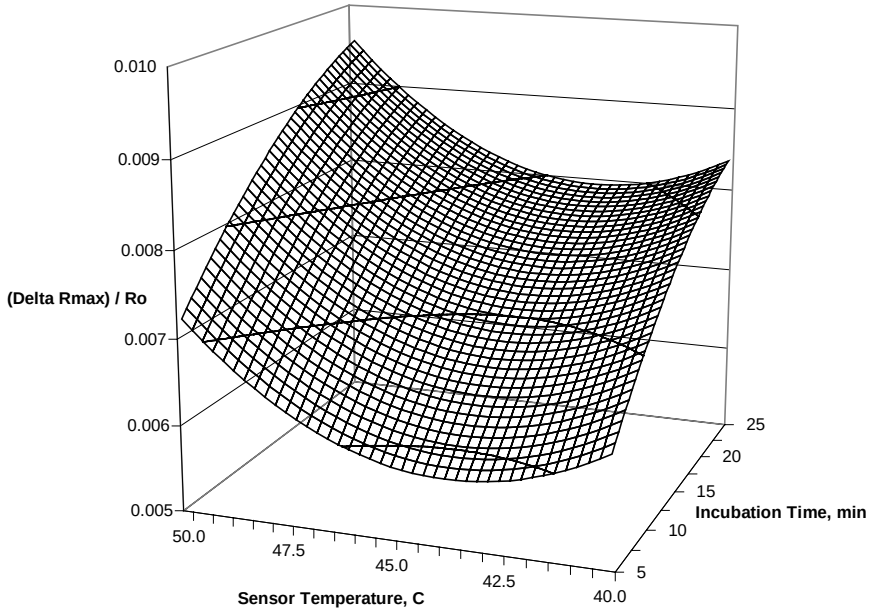

**AlphaM.O.S. Fox 3000 - Sensor 1**
**Incubation Temperature = 75C**

4



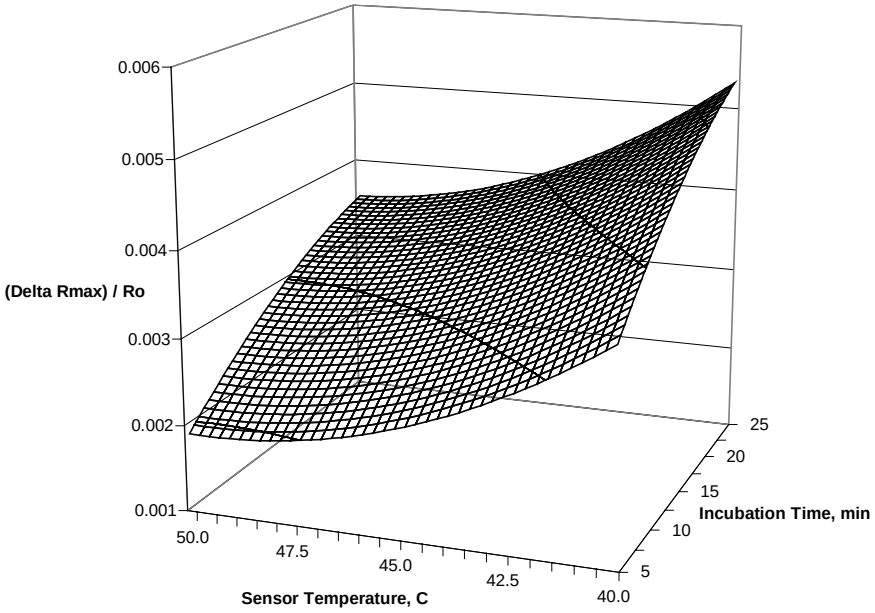

**AlphaM.O.S. Fox 3000 - Sensor 10**
**Incubation Temperature = 75C**

5



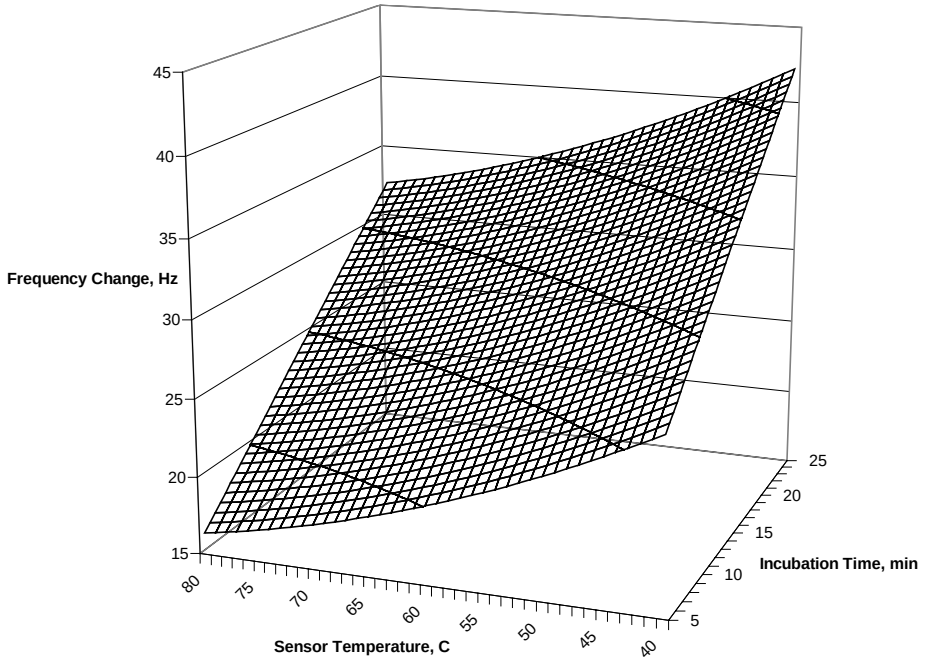

**Cyranose 320 - Sensor 10**
**Incubation Temperature = 100C**
**Pump Speed = Low (50 cc/min)**

6



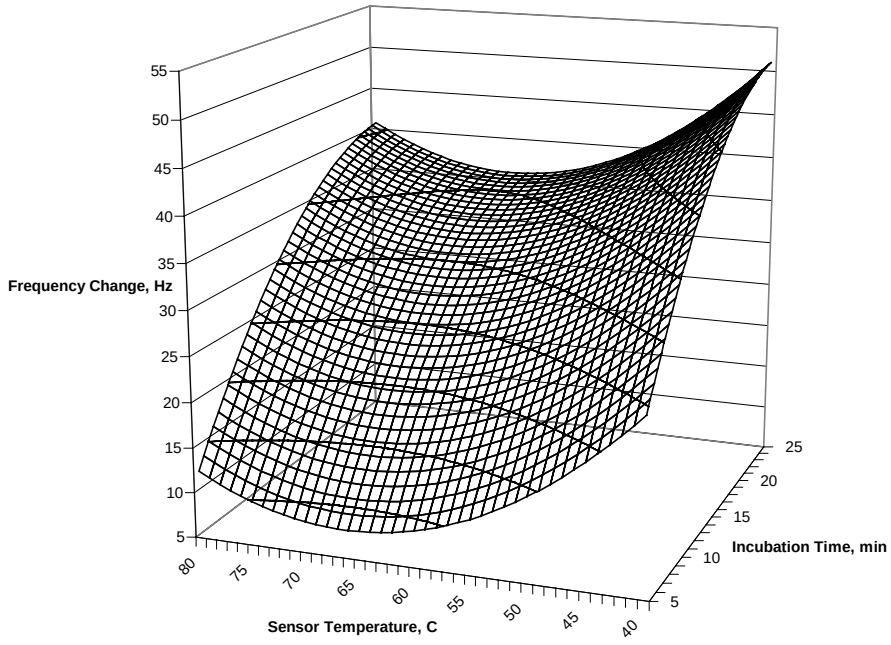

**Cyranose 320 - Sensor 22**
**Incubation Temperature = 100C**
**Pump Speed = Low (50 cc/min)**

7



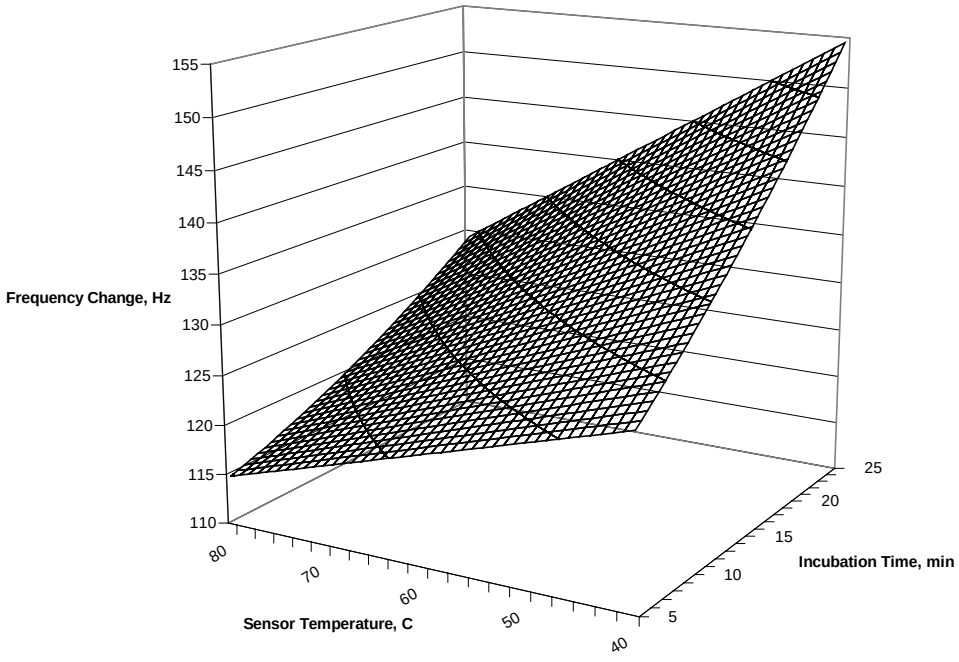

**QMB6 - Sensor 1**
**Incubation Temperature = 100C**

8



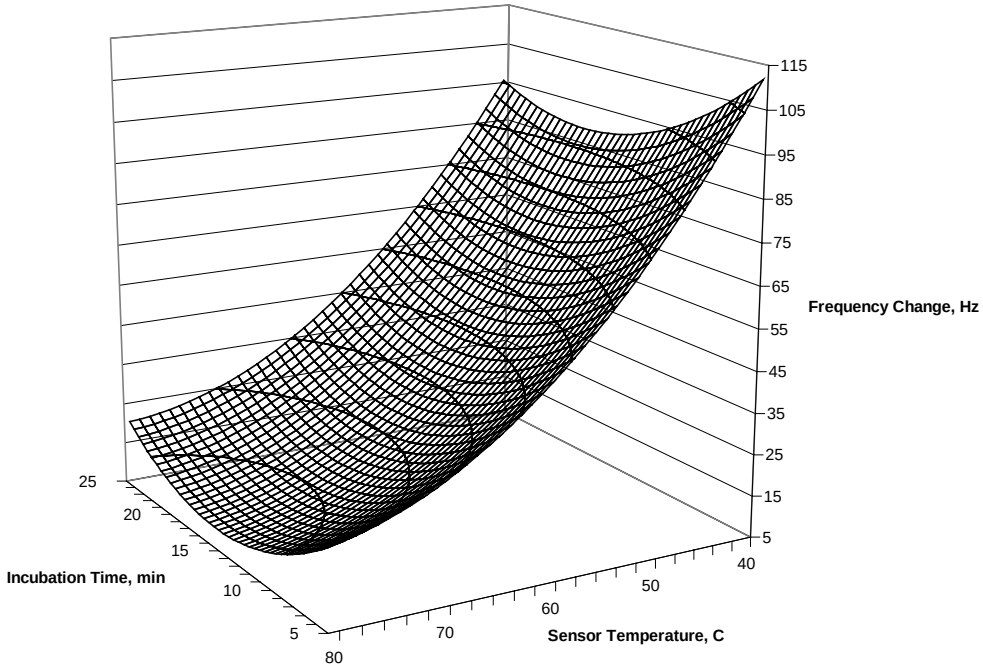

**QMB6 - Sensor 2**
**Incubation Temperature = 100C**

9



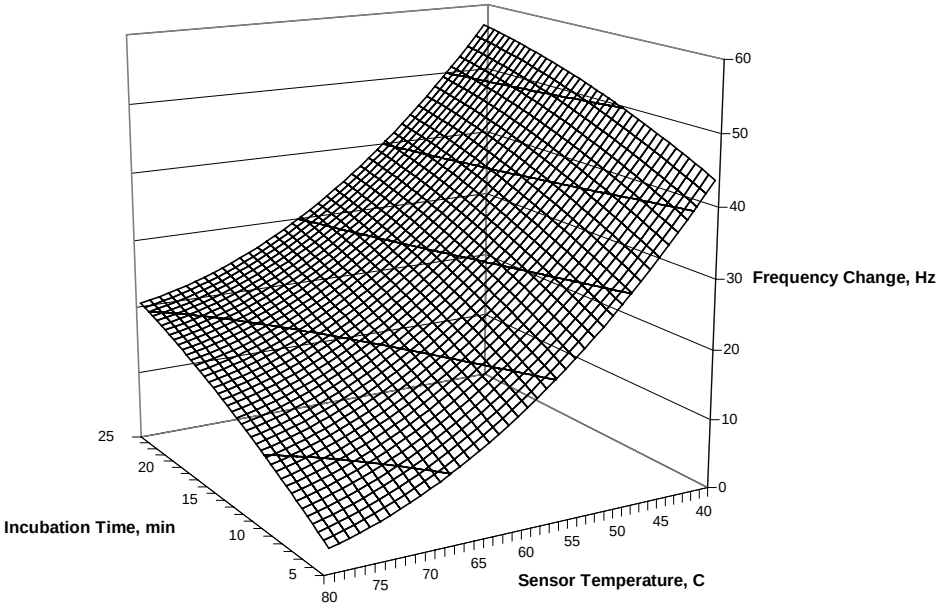

**QMB6 - Sensor 3**
**Incubation Temperature = 100C**

10



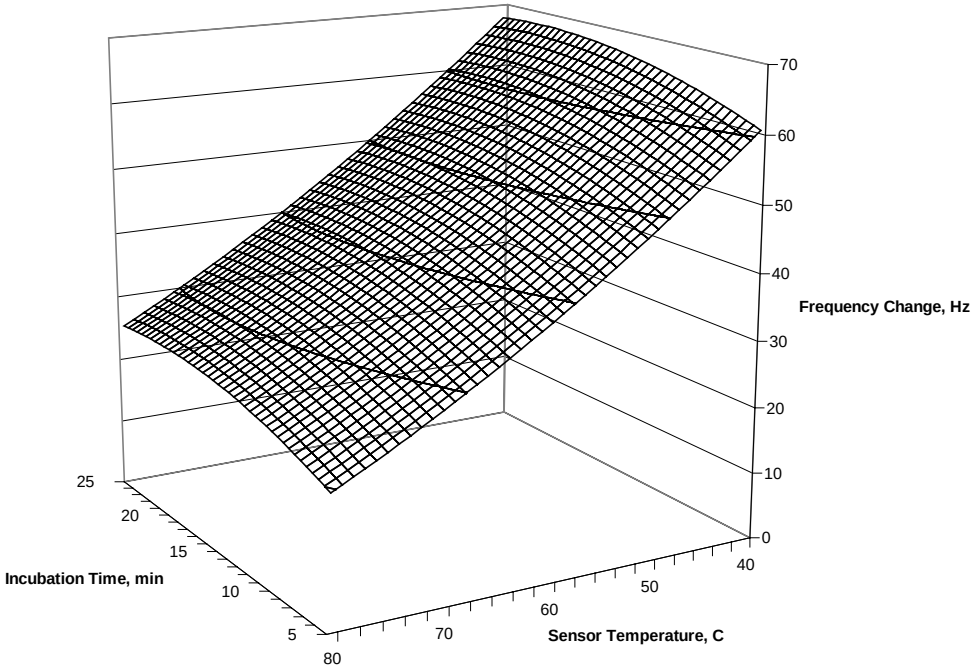

**QMB6 - Sensor 4**
**Incubation Temperature = 100C**

11




**QMB6 - Sensor 5**
**Incubation Temperature = 100C**

12




**QMB6 - Sensor 6**
**Incubation Temperature = 100C**

13

**Chapter 4**

Journal of Food Science

# COMPARATIVE PERFORMANCE ANALYSIS OF THREE ELECTRONIC NOSE SYSTEMS USING DIFFERENT SENSOR TECHNOLOGIES IN ODOR ANALYSIS OF RETAINED SOLVENTS ON PRINTED PACKAGING

D. Van Deventer — Graduate Student
P. Mallikarjunan * — Assistant Professor
Biological Systems Engineering, VPI&SU, 200 Seitz Hall, Blacksburg VA 24061-0303

Corresponding Author: Dr. Parameswarakumar Mallikarjunan
200 Seitz Hall, Blacksburg, VA 24061-0303
Ph: 540 231 7937 Fax: 540 231 3199 E-mail: kumar@vt.edu

**Optimization of Chemosensory Systems**
**Food Engineering and Physical Properties**

**ABSTRACT**:
The food industry is interested in determining the applicability of using electronic nose instrumentation for odor analysis of retained solvents on packaging. Performance analyses of electronic nose systems using three leading sensor technologies showed that the conducting polymer sensor technology demonstrated the most discriminatory power, while all three proved able to discriminate among film samples at varied levels of retained solvents. All three systems correctly identified 100% of unknown samples. Based on discriminatory power and practical features, the FOX 3000 and the Cyranose 320 were superior. The results indicate that electronic nose instrumentation can be used as a complimentary discriminatory tool in quality control for packaging.

**Keyword(s)**: electronic nose, retained solvents, response surface analysis, printing inks, polymer films

## INTRODUCTION

Changes in product quality and flavor due to aroma absorption and the transfer of undesirable volatiles from packaging to foods are important mechanisms of deterioration when foods are packaged with polymer-based materials. This transfer of volatiles may lead to off-odor and off-taste development (Hotchkiss, 1997). From an industry perspective, high levels of retained printing solvents on packaging pose both a qualitative problem from the development of off-odors and a potential safety problem regarding the migration of ink plasticizers. Thus, the migration of compounds from the packaging to the product is a major concern from both toxicological and sensory viewpoints. Some compounds of particular concern include phthalates and adipate plasticizers, and the alcohol and ketone solvents used predominantly throughout the printing industry (Robertson 1993; Sharma and others 2000).

The electronic nose is an instrument that begins to bridge the gap between analytical techniques such as gas chromatography (GC) and sensory analysis. The monitoring of the level of retained solvents is the primary method of quality control of packaging after printing. Current quality assurance techniques use sensory analysis, GC, GC-olfactory, and GC-mass spectroscopy. While these methods are useful research tools, they require extensive time and preparatory measures, and expertise in understanding the results. If an electronic nose could be demonstrated to be effective in this application, it could become a complimentary tool in quality assurance.

Diffusion is the primary mechanism for the transfer and migration of chemical compounds from packaging materials to food. Free volume theory asserts that molecular motion in the bulk state occurs due to the presence of holes or voids. This is the most prevalent theory explaining the diffusion of molecules through solid materials (Ozdemir, and others 1999). Additives used in the production of plastics used in food packaging to enhance their physical properties tend to migrate from the plastics due to their high mobility and low molecular weights. Possible migrants from plastics could be monomers, oligomers, plasticizers, antioxidants, antistatic and antifogging agents, colorants, emulsifiers and degradation products. Sources of compounds that may migrate into food from plastic films include ink solvents, adhesive systems used in laminations, and polymerization reactions in which a solvent is used as a reaction medium. Migrating solvents such as abietic acid, toluene, butanone-2, ethyl acetate, and hexane

are particular concern as well as pigments such as molybdate orange (Gilbert and others 1988; Ozdemir and others 1999).

Castle and others in 1989 demonstrated that on polypropylene packaging, transfer of components from the ink on the outer surface of the film to the inner food contact surface occurred amounting to 6 % of the total amount of plasticizer used in the printing system for dicyclohexyl phthalate. It was also found that in each case of retail food samples that were tested, blank foods had negligible plasticizer levels and the packaged foods had plasticizer levels corresponding to those found in the packaging material (Nerin and others 1993).

The objective of this work is to analyze and compare the performance of three electronic nose systems as a complimentary analysis tool for quality control of retained printing solvents in packaging. The null hypothesis is that none of the instruments are yet suitable for this application.

## MATERIALS & METHODS

This study involves performance analyses of these electronic nose systems to be used as a complimentary rapid analysis tool in conjunction with current instrumentation used in the quality control of packaging films. The objectives of this work are to determine which, if any, is the most appropriate sensor technology for this application, and which, if any, of the systems are most capable in discriminating between sample classes and correctly identifying unknown samples.

### *Electronic Nose System Information*

Three electronic nose systems using different sensor technologies, metal-oxide semiconducting sensors, conducting polymer sensors, and quartz microbalance sensors, were used in a performance analysis in the application of detecting food packaging taints. A sample headspace is generated and then passed through a sensor chamber by either pressurizing the headspace with a carrier gas or by drawing the headspace aromas with a pump. The sensor array in the chamber then interacts with the complex aroma and the response of each sensor in the array together form a characteristic recognition pattern for that sample. Statistical analyses such as Principal Component Analysis (PCA) and or Canonical Discriminant Analysis (CDA) are then used to discriminate and group samples, or to identify an unknown by comparing its characteristic recognition pattern to a known database. To effectively develop a database, each

electronic nose must be trained with samples that have known values, or values that are correlated to some other analytical means.

The metal oxide semiconducting sensor based system examined was the Alpha M.O.S. Model FOX 3000 (Alpha M.O.S., Toulouse, France). This system has 12 sensors with different metal oxide coatings that vary in sensitivity and selectivity. The interaction of the sensors with compounds in the sample aroma is measured as a function of the change in the conductivity of the sensor. The maximum change in resistance of each of the sensors was the measurement taken by the instrument to be used in this analysis. It is connected to an automatic headspace sampler Model HS50 (Alpha M.O.S., Toulouse, France) and uses 10 mL headspace vials with nitrogen as the carrier gas.

The conducting polymer sensor based system examined was the Cyrano Sciences (Pasadena, CA) handheld Cyranose 320 unit. This system has 32 sensors each coated with a unique carbon-black polymer film. This system is a hand-held unit and was operated manually using a tripod and a heating block to analyze headspace aromas in 10 mL headspace vials. The heating block used was a Reacti-Therm Heating Module (Pierce Chemical Co., Rockford, IL). The interaction of the sensors with compounds in the sample aroma is also measured as a function of the change in the conductivity of the sensors for this instrument as well. The values taken for analysis in this system were the maximum change in resistance divided by the original resistance value. The carrier gas in this case is ambient air. As per the user manual's recommendation, the carbon and silica gel filters were not used due to the nature of the laboratory environment and low moisture content of the samples.

The quartz-microbalance based system examined in this preliminary work was the HKR Sensorsystems Model QMB6 (Munich, Germany). The system was connected to an automatic headspace sampler (Model HS-40, Perkin-Elmer LLC, Norwalk, CT) as well as an external heat exchanger and chilling unit. The external heat exchanger and chilling unit were used to overcome temperature control difficulties due to the close proximity of the sensor and sample heating chambers. This electronic nose consists of a series of six unique non-selective sensor elements that are coated with gas chromatographic stationary phases of varying polarities. The interaction of the sensors with the compounds in the sample aroma is measured as a function of the change in oscillating frequency of the sensors. The system uses 21 mL headspace vials and nitrogen as the carrier gas. The sensors are oscillated at 10 MHz. The adsorption of volatiles

from the sample headspace onto the sensor causes a change in the mass of the sensor that results in a measurable change in its oscillating frequency. The resolution of the sensors is ±1 Hz (Perkin-Elmer QMB6 Operators Manual, 1999).

The three electronic nose systems were tested at optimum settings determined in previous work. These settings include a universal sample incubation time of 5 minutes for all three systems.

*Sample Preparation Methodology*

The samples used in this research were classified prior to electronic nose analysis by means of gas chromatography (GC) analysis using the quality assurance procedure of the manufacturer. The volatile compounds of interest cannot be specifically identified due to a binding confidentiality disclosure agreement with the supplying manufacturer and specific information related to the procedure cannot be shared, although the nature of the retained compounds of most concern are alcohols and ketones (Robertson 1993). Each aspect of this study used samples available from a total of ten film products. For the benefit of the reader the results of the GC analysis are given for the samples in terms of an unspecified threshold level, X, dividing 'conforming' retained solvent levels from 'non-conforming' retained solvent levels. The levels of the films used in the research were 0.12X, 0.23X, 0.23X, 0.42X, 0.24X, 0.58X, 1.28X, and 1.53X for the first eight samples. These samples were identified as samples 1-5, and 6A-6C respectively. In all electronic nose analyses, ten observations were taken from each of the ten available film products.

The last three sample levels given, samples 6A-6C were the samples used in the first part of the electronic nose study, which involved the discrimination of three levels of retained solvents for a single product. Databases were developed using ten replications from each product category.

The second part of the research involved the discrimination of assorted 'conforming' and 'non-conforming' films. The first six samples, 1-6A, were used to develop the 'conforming' films database, and samples 6B and 6C were used to develop the 'non-conforming' films database. The remaining two available film products were withheld from the construction of the database to be used as unknowns. They were found to have retained solvent levels of 0.12X and 0.20X, indicating that they should both be identified as 'conforming' by the electronic nose. Databases were developed using all ten replications from the products used except for the

Cyranose 320 system. This system has the limitation of having a maximum of ten observations in each class. Consequently for the 'conforming' database, one observation was taken from samples 1-6A, and a second observation was taken at random from four of the classes to reach a total of ten observations. For the 'non-conforming' database, five observations were taken from each of the available 'non-conforming' films, samples 6B and 6C.

The film samples used in the assorted products part of the study were printed using either flexography or rotogravure printing and the materials included OPP, metallized-OPP, polyester, LDPE, and coated paper. These packaging products are used with snack food products.

The packaging samples used for discrimination analyses of three levels of retained solvents were a two-layer polymer film. The product was rotogravure reverse printed with approximately 375% ink coverage onto a layer of oriented polypropylene and then laminated onto a layer of low-density polyethylene using a water-based adhesive. Control aromas were tested using the base materials present before printing. These included air samples, and unprinted samples of oriented polypropylene and low-density polyethylene.

Each sample vial tested in this work was prepared by removing a 51.6 $cm^2$ (8.0 $in^2$) section from the printed product impressions and folded into the appropriate headspace vials.

*Statistical Analyses*

Multivariate discriminant analysis was performed on the data obtained from each electronic nose system using the software associated with each system. These include AlphaSoft v 7.01 (FOX 3000), PCNose v. 6.5 (Cyranose 320), and QMBSoft v. 1.22 (QMB6). In addition the PROC CANDISC, DISCRIM, and PRINCOMP procedures in the statistical software package PC-SAS (SAS Inc., Cary, NC) were also used to perform canonical discriminant analysis and principal component analysis to obtain additional information. The PROC STEPDISC in SAS was also used to rank sensor data based on the contribution to the discriminatory power of the system.

*Procedure*

First, the system technologies were compared using an equal number of sensors, samples, and observations from each system. The FOX 3000, Cyranose 320, and QMB6 systems have 12, 32, and 6 sensors respectively. The stepwise discriminant analysis procedure in SAS, PROC STEPDISC, was used rank the sensors in each system with a significant F-statistic at a preset $\alpha$-level of 0.05. Also, the stepwise method within the PROC STEPDISC procedure was used to

ensure that only independent variables were chosen. This method removes a variable or sensor if multiple-linearity develops with other variables to the extent that its F-statistic is no longer significant at the prescribed $\alpha$-level.

Each system was used to test ten samples of three different film classes with varying retained solvent levels. The precise values of retained solvent levels cannot be reported here due to a binding disclosure agreement. However, these values were determined through gas chromatography analysis to be 0.58X, 1.28X, and 1.53X, given that X is the threshold total retained solvents level above which a printed film is deemed to be 'non-conforming'. Canonical discriminant analysis, a common form of multivariate factor analysis used in these systems, was performed on the data obtained from four sensors using the SAS PROC CANDISC and PROC DISCRIM procedures. Then, an analysis of the discriminatory power, as affected by the number of independent sensors in each system, was made.

Next, an analysis of the discriminatory power between three levels of films was examined using both the software for each system, and the independent SAS software. In order to test the discriminatory power of each system, ten observations were made using the same three sample groups having different levels of retained solvents, and each was first analyzed according to the statistical method used by its own software. This information was then used to examine the performance of the each system. To investigate more objectively, third-party software, SAS, was used first to perform PCA to reduce the number of factors to an even unbiased amount and then to perform a CDA that would have descriptive statistics that could be used to compare the three systems.

Another analysis of the discriminatory power of each system was then performed using assorted 'conforming' and 'non-conforming' products and unknowns. To examine these three systems in this respect, a database was developed using assorted packaging products. Two packaging products were withheld and tested as unknowns to each electronic nose instrument. The packaging products were classified prior to electronic nose analysis as being 'conforming' or 'non-conforming' based on standard gas chromatography analysis performed in the industry. The packaging products used to compose the 'conforming' class were found to have retained solvent levels of 0.12X, 0.23X, 0.23X, 0.42X, 0.24X, and 0.58X, given that X is the threshold level dividing 'conforming' products from 'non-conforming' products. The packaging products used to build the 'non-conforming' class in each database were found through gas

chromatography analysis to have retained solvent levels of 1.28X and 1.53X, and the unknowns that were tested had retained solvent levels of 0.12X and 0.20X indicating that they should both be identified as 'conforming' if the electronic nose instruments were to be correct. Finally, an instrument recommendation was developed.

## RESULTS AND DISCUSSION

The data obtained from these experiments was used to make an objective comparison of the three sensor technologies being examined and a performance comparison of the three electronic nose instruments used. These technologies were compared by determining which technology discriminated most between three levels of one packaging product using an identical numbers of sensors from each system. The comparison of the complete systems was based on the discrimination of three levels of one product, discrimination among assorted 'conforming' and 'non-conforming' products, and identification of unknowns.

The control aromas tested including air samples, and unprinted samples of oriented polypropylene and low-density polyethylene. The results demonstrated that the predominant source of volatiles in the sample aromas was the printed material. The response signals for the control films were all near the air samples and away from the printed samples on canonical discrimination plots for each system. The raw sensor values for the air and blank materials were all at minimal levels supporting the assumption that the volatile fraction of the samples of interest was primarily from the printed material.

### *Technology Comparison*

To objectively compare the sensor technologies and not the systems themselves, it was necessary to use independent statistical analysis software (SAS) and to establish a uniform set of experimental parameters including the use of an equal number of independent variables or sensors.

Using the PROC STEPDISC procedure in SAS, it was determined that for an $\alpha$-level of 0.05, four sensors were significant to the discriminatory model for the FOX 3000, ten sensors for the Cyranose 320, and four sensors for the QMB6. Consequently, it was chosen to use the four sensors from each system most significant to the discriminatory model to objectively compare the discriminatory power of each technology in analyzing retained solvent levels on printed packaging films.

These multivariate statistic analyses were performed on the obtained data with the results given in Table 1 and Table 2. The ability of the three different sensor technologies to discriminate between the three classes of samples is compared using CDA plots, the Wilks' lambda value, the F-statistic for the Wilks' Lambda value, the percent correct during cross-validation of the classes, the Mahalanobis distances separating the groups, and the F-statistics for the Mahalanobis distances. The CDA plots using the data from four sensors is given in Figure 4, Figure 5, and Figure 6 for the metal-oxide semiconducting sensor technology, conducting polymer-composite sensor technology, and quartz microbalance sensor technology, respectively.

The Wilks' Lambda value is calculated from the inverse of the product of each of the eigenvalues incremented by one. Because lambda is a kind of inverse measure, values of lambda that are near zero denote high discrimination between groups. The F-value for the Wilks lambda provides a quantitative value for the overall discrimination of all the classes involved in the discriminant analysis. While it is a useful number for quickly quantifying the amount of separation between classes, it denotes total discrimination and does not indicate if the total amount of separation is due to a balanced separation of all the classes or a very large separation of some classes while having little separation between other classes.

Mahalanobis distances, D, examine variance among samples within a group and also the covariance among groups. The Mahalanobis distances are calculated in units of standard deviation from the group mean. Therefore, the user can then assign a statistical probability to that measurement. For a relatively large number of observations and multivariate normal distribution, D/2 behaves like a normal multivariate z with standard deviation 1. In theory, D/2 can be examined to obtain an indication of the separation between samples and their estimated populations, and the probability of incorrect assignment. A D value of 5 would correspond to about 5 standard deviation separations, which covers approximately 99% of a population, given a multivariate normal distribution. Separation of groups quantified with a Mahalanobis distance greater than 5 would indicate very little overlap. In practice, the determination of the cutoff value depends on the application and the type of samples (Jolliffe 1986; Marcus 2001). The value of 5 is used here as the cutoff for being classified as being part of a group or being separate from it. Typically, the Mahalanobis distances could not be compared from system to system as it can be a biased number depending on the number of observations taken, sample classes used, and the number of independent variables. However, for this technology comparison, four

independent variables, three classes, and 30 observations were used for each system, so the Mahalanobis distances may be compared to determine which technology achieved better separation.

The F-value incorporates the Mahalanobis distance and also takes into account the number of observations used, the degrees of freedom, and the number of independent variables used to determine if two classes are significantly different. These F-values for the Mahalanobis distances give a standardized value of the separation between each of the three classes analyzed in the discriminant analysis. The percent correct during cross-validation also provides additional information regarding the degree of separation. After the discriminant model is developed, each data point is removed and tested as an unknown to the model developed with the remaining data points. A value of 100% indicates complete separation of all classes. A value of 90% is usually considered sufficient for a database model and is the value used here. The user based on the application requirements sets the actual value.

In examining the results shown in the CDA plots given in Figures 4, 5, and 6, it is clearly seen that the conducting polymer-composite sensor technology shown in Figure 5 provides the strongest discrimination between the three class levels of retained solvents for this particular film product. Figures 4 and 6 show that the remaining two sensor technologies also provide distinct separation among the three classes although which sensor technology provides better discrimination cannot be concluded without examining the quantitative data from the discriminant factor analysis given in Tables 1 and 2.

In examining the results shown in Table 1 and Table 2, the Mahalanobis distances between classes are clearly the greatest for the conducting polymer-composite technology. The Mahalanobis distances for the remaining technologies show that the metal-oxide semiconducting sensors show discrimination of the classes on the same order as the quartz microbalance sensors. The separation between the 'conforming' class 1 and the remaining 'non-conforming' classes is greater for the metal-oxide sensors while the separation between the two 'non-conforming' classes is greater for the quartz microbalance sensors. The Mahalanobis distances reported in the Tables 1 and 2 were calculated as $D^2$. Therefore using a cutoff value D of 5, the minimum distance in the tables that would indicate a group separation of at least 99% would be 25. All values shown for each system in these tables are greater than 25 and so it must be concluded that

using four sensors, all three technologies could discriminate effectively between the film samples with three different levels of retained solvents.

The F-values for each of the Mahalanobis distance support the conclusions previously stated. All of the F-values were significant with p-values less than 0.0001 indicating that the null hypothesis with a preset alpha of 0.05 must be rejected, and that the hypothesis that the groups are significantly different should be accepted. The Wilks' Lambda values are less than 0.02 further indicating the class separation first shown in CDA plots. The Wilks' Lambda is somewhat akin to a $1\text{-}R^2$ value indicating the overall fit of the discriminatory model with values closer to zero. The model for the metal-oxide semiconducting sensors has a fit greater than 98% while the remaining two systems are fitted at values greater than 99%. The percent correct during cross-validation also show that all three technologies can discriminate the classes well. The conducting polymer-composite sensors demonstrate complete discrimination with a value of 100% correct. The remaining two technologies demonstrate near complete discrimination with a value of 96.7% correct. The most likely reason for a misclassification rate of 3.3% is simply that a value on the edge of one class grouping, when removed shrinks the area for that group and now as an unknown falls in between that group and another. It then must be classified with the nearest group and stands a chance of being misclassified. A correct classification rate greater than 90% again supports the conclusion that all three systems have sufficient discriminatory power for this application.

It must be concluded based on the separation of the three retained solvent levels for this film product, that the conducting polymer-composite sensor technology offers the greatest discriminatory power. It must also be concluded that all three sensor technologies offer sufficient sensitivity and selectivity to demonstrate effective discriminatory power in this application.

*Recommendation of Sensors*

It may be desired to develop an application specific electronic nose for analysis of retained solvents on packaging. For an application specific electronic nose, only the sensors that provide the fundamental discriminatory power for that application are desired. It was found that for the metal-oxide sensor unit, a machine could be developed using only sensors 1, 6, 4. Using these sensors results in F-values of 42.5, 153.1, and 44.0 for Mahalanobis distances between classes 1 and 2, 1 and 3, and 2 and 3, respectively. These values result in the greatest minimum

separation of any of the classes as compared to using any number of combined sensors from the original system. For the conducting polymer sensor system, an effective machine could be developed using only sensors 6 and 22. Using only two sensors is a subjective decision. However, it provides the strongest level of discrimination until 10 sensors are used. The level of discrimination using the two sensors is more than adequate resulting in F-values of 419.9, 890.1, 463.0 for the Mahalanobis distances and a Wilks' Lambda of 0.0006 for the full discriminatory model. For the quartz microbalance sensor based unit, it was found that the use of sensors 5, 3, and 2 could be used to develop an effective machine for this application. The combination of these three sensors provide F-values of 32.5, 148.8, and 78.2, which are the greatest for any sensor combination with a Wilks' Lambda value less than 0.07 for the entire model.

These selections were determined by first ranking the sensors in the system based on their contribution to the overall discriminatory power of the system. Discriminant analyses were performed first using only the most significant sensor, and then repeated, each time adding the next most significant sensor. Because some sensor combinations resulted in better discrimination among some classes and other sensor combinations resulted in better discrimination among the remaining groups, additional discriminant analyses were performed. These analyses were performed after removing one of the classes to examine the significance of each sensor in discriminating between the classes left remaining. Additional sensor combinations were selected for discriminant analysis from these results. This resulted in a more optimal sensor combination for the quartz microbalance system only. The optimal sensor combinations for the remaining two systems were selected from combinations derived from the original set of discriminant analyses using all the classes. The aforementioned sensor combinations were selected based on criteria requiring maximum discriminatory power (particularly between 'conforming' and 'non-conforming' classes) obtained with a minimal number of sensors.

*Instrument Comparison: Discriminatory Power – Single Film Sample 3 Levels*

The AlphaSoft v. 7.01 software used by the FOX 3000 performs a straight discriminant factor analysis (DFA) or CDA on the data obtained from its 12-sensor array. The results of this analysis are illustrated in Figure 7. This plot shows that the three classes are well separated visually. The graph gives Variance proportions for the canonical factors 1 and 2 of 84.90 and 15.10 and a Euclidean Distance of 0.2546, 0.6784, 0.4243, for interclass distances between

classes 1 and 2, 1 and 3, and 2 and 3, respectively. It is easier to conclude visually from the graph that separation is achieved than it is to use the reported Euclidean distance values. Without the graph it is not possible to note the variation of one group with respect to the location of the gravity center of another group by examining the Euclidean distances alone. Generally, the higher the Euclidean distances, the greater the group separation. Therefore, it is seen that the system most discriminates between class 1 and class 3. The percent recognition during cross-validation was reported to be 87%. This value is slightly less than the 90% value desired to indicate good class separation in a model. To gain additional quantitative and descriptive information, a second analysis using SAS was performed. Using the PROC CANDISC and PROC DISCRIM procedures, a CDA was performed on the data from the 12-sensor array. The variance proportions held by each of the canonical factors were found to be 84.90 and 15.10, which are identical to the values calculated by AlphaSoft. The CDA plots from both analyses were also found to be identical. From this it is reasonable to conclude that the analyses methods and procedures were the same, (AlphaSoft probably uses a similar algorithm), and that the descriptive data obtained through SAS is relevant. The Mahalanobis distances, $D^2$, and $F_{Mahalanobis}$ statistics between classes 1 and 2, 1 and 3, and 2 and 3, were reported by SAS to be 105.8, 210.5, 62.2 (Mahalanobis), and 26.1, 52.0 15.4 (F-statistic), respectively. Although the Mahalanobis distances are large, with a minimum value of 10.28, these numbers do not provide much information as the Mahalanobis number becomes biased if the number of independent variables is high relative to the number of sample observations. With 12 independent variables (sensors) and 10 observations in each of three classes, it is more reasonable to examine the $F_{Mahalanobis}$ statistics. These values do confirm the class separation shown in Figure 7 as each F statistic was found to be significant with a p-value less than 0.0001. Wilks' Lambda was reported to be 0.0031 indicating a model fit greater than 99% and its F statistic 22.8 was also significant with a p-value less than 0.0001. The descriptive statistics, and particularly the plot, obtained from the AlphaSoft and SAS software indicate that the FOX 3000 achieves good discrimination among the three levels of retained solvents for this product and has shown potential as a useful tool in this application.

For the Cyranose 320, the canonical discriminant analysis performed by its PCNose v. 6.5 software is performed after using PCA to derive a number of principal components from the original 32 sensors. This is done to avoid over fitting of the discriminant model and to reduce

the number of independent variables thereby making the calculations in the analysis manageable and the Mahalanobis distances meaningful. Figure 8 shows the CDA plot from Cyrano Sciences PCNose software of the three classes of samples. The software reports Mahalanobis, D, interclass distances of 15.143, 24.053, 14.360 for classes 1 and 2, 1 and 3, and 2 and 3, respectively as well as a percent recognition during cross-validation (leave one out method) of 100%. The value of 100% supports the visual illustration provided by Figure 8 that shows excellent separation. All of the Mahalanobis values are considerably greater than 5, further indicating very good separation. Again it was attempted to use SAS to gain additional information. This information was successfully obtained using the PROC PRINCOMP, then PROC CANDISC and PROC DISCRIM procedures on the first four principal components containing, 99.63% of total variance. Mahalanobis interclass distance (D) values were calculated that were identical to those calculated by the PCNose software with some very minor discrepancies attributed to rounding differences between the two software systems. From the equivalence of the D values, it was concluded that the remaining statistics calculated using SAS were also relevant. The F-statistics calculated by SAS were 252.0, 640.8, and 230.4, for the Mahalanobis distances between classes 1 and 2, 1 and 3, and 2 and 3, respectively. The Wilks' Lambda for the model was calculated to be 0.0004 with an F statistic of 265.2 with a p-value less than 0.0001. The Wilks' Lambda indicates a model fit greater than 99% and the extremely high $F_{Mahalanobis}$ statistics support the conclusions of excellent separation between groups. It is also seen that the $F_{Mahalanobis}$ statistics are generally on the order of being 10 times greater than those seen for the FOX 3000 indicating that the Cyranose 320 achieves considerably better discrimination among the three classes. The Mahalanobis interclass distances are not directly comparable to the FOX 3000 system because a different number of independent variables were used in each analysis.

For the QMB6 system, Figure 9 shows the DFA or CDA results using the data from its 6-sensor array as analyzed by its software QMBSoft v. 1.22. The plot itself visually shows very good separation among the groups, although this version of the software does not provide standardized values for the canonical factors along the axes. While the software does provide several descriptive statistics such as Mahalanobis distance and class matching coefficients when analyzing unknowns, it does not provide such information with this version of the software regarding interclass information of database validation. Therefore, it was again attempted to use

SAS to gain additional information. Using the PROC CANDISC and PROC DISCRIM procedures on the data from the six-sensor array, additional information was successfully obtained. The CDA projection plot was visually identical to the one provided by the QMBSoft software. On that basis, it was deemed that the remaining descriptive statistics provided by SAS were valid. Mahalanobis interclass distance ($D^2$) values were calculated to be 31.8, 109.0, and 96.8, for classes 1 and 2, 1 and 3, and 2 and 3, respectively. These values indicate D values greater than 5 when the square roots are taken, and support the visual conclusions made using Figure 9, that the QMB6 system also achieves good separation among the three classes. The F-statistics calculated by SAS were 21.6, 74.0, and 65.7, with p-values less than 0.0001 for the Mahalanobis distances between classes 1 and 2, 1 and 3, and 2 and 3, respectively. The Wilks' Lambda for the model was calculated to be 0.0060 with an F statistic of 43.7 with a p-value less than 0.0001. The Wilks' Lambda indicates a model fit greater than 99%. The percent recognition during cross-validation was found to be 96.7% which is greater than the 90% value set as a criterion. It is also seen that the $F_{Mahalanobis}$ statistics are generally on the order of being ten times less than those found for the Cyranose 320 and on the same order as those found for the FOX 3000. This indicates that while all three systems achieved good separation, the Cyranose 320 achieves considerably better discrimination than the other two systems. Again, the Mahalanobis interclass distances are not directly comparable among the three systems because a different number of independent variables were used in each analysis. However, the $F_{Mahalanobis}$ statistics for the QMB6 show that it achieves slightly worse than discrimination than the FOX 3000 between classes 1 and 3, and better discrimination between the remaining classes. Overall, the discriminatory power of the FOX 3000 and the QMB6 were comparable in this analysis.

Independently developed software, SAS, was then used to perform an objective analysis of the three systems by first reducing the number of variables to an equal number through PCA and then compared using the PROC CANDISC and PROC DISCRIM. While this method does not mimic the statistical analyses methods used by all three systems, it provides a legitimate method and descriptive statistics that will be directly comparable for the three systems. The results of the PCA procedure are given in Table 3 where it is seen that for all three systems, the first four principal components carried at least 99.5% of the total variation. Principal component analysis usually preserves most of the total variation in the system in the first few principal components. Consequently, only a small fraction of the variation that may contribute to the

discriminatory power of the CDA is lost. However, it should be noted that principal component analysis only develops principal components or axes based on the total variation among observations within a system. These axes may or may not be the axes that provide the most discrimination among pre-grouped classes of samples. Subsequently, the first four principal components were used in the SAS CDA procedures. The descriptive statistic results for the three systems are given in Table 4 and Table 5 and SAS CDA projection plots are given by Figure 10, Figure 11, and Figure 12 for the FOX 3000, Cyranose 320, and QMB6 systems, respectively.

These results are very similar to those found when only four sensors were used to compare the technologies used by each system. All three systems achieved good separation of the three classes supported by minimum Mahalanobis interclass distances (D) greater that 5, although again the Cyranose 320 showed considerably better discrimination than the remaining two systems. It should also be noted that using this method the FOX 3000 system now achieved 100% recognition during cross-validation indicating complete separation of the groups. Overall the results from this objective SAS support the conclusions previously made that the Cyranose 320 showed the greatest discrimination, while the remaining systems showed efficient discrimination on the same order.

*Instrument Comparison: Discriminatory Power – Assorted Films & Classification of Unknowns*

The first step in determining if an electronic nose system is useful in an application is to determine if a database that sufficiently discriminates between classes can be developed. However, it simply does not mean that the equipment is sufficiently effective until it can be shown that unknowns can be accurately classified with an efficient rate of success. If an electronic nose is to be used, as a rapid analysis tool for complimentary analysis to bridge the gap between sensory analysis and analytical techniques, a quick simple method is ultimately desired. This would involve using a minimum of databases, preferably one, to classify an assorted range of products with unknown ('conforming' or 'non-conforming') levels of retained solvent odors.

For the FOX 3000, there is no limitation on the number of observations that may be used in a database class. Therefore, 10 observations were taken from each sample in order to build the classes. The AlphaSoft software was used to analyze the results and to classify unknowns. Figure 13 shows the obtained DFA (CDA) plot. It can be visually determined from this plot that there is a slight overlap of groups indicating a possibility of some unknown samples being

classified as 'confused' if they were to fall in that region. The reported percent recognition (leave one out method) during cross-validation was 90% indicating that the database was valid. The reported Euclidean distance between groups of 0.8727 was high (close to 1) indicating in one respect that there was significant group separation. Again SAS was used to gain additional information and its results regarding identical percent variance carried by the canonical factors (C1 100% variance) and identical CDA plots indicated that the additionally reported results were valid. The CDA method using SAS reported a Mahalanobis interclass distance, $D^2$, of 25.7, with an $F_{Mahalanobis}$ of 29.1 significant with a p-value less than 0.0001. The reported Wilks' Lambda was 0.1807 with an F-statistic of 29.10 significant with a p-value less than 0.0001. The model fit therefore is approximately 82% with the lower value attributed to the increased variance expected when using assorted films. The most important indication of the system's usefulness however is the correct classification rate of the unknowns. Table 6 provides the results of the unknown analyses as performed by AlphaSoft Software. This software does not use the minimum Mahalanobis distance to classify unknowns and instead uses the percent recognized. Table 6 shows that the AlphaSoft software correctly identified 100% of both the unknowns if forced to choose between the two classes and 100% correct for Unknown1 and 95% correct for Unknown2 when it was allowed to choose 'unknown' (meaning a sample was not considered close enough to either class to be recognized). The average percent recognition among the ten observations was 87% for Unknown1 and 94% for Unknown2. From these results, it is concluded that the FOX 3000 is suitable for this application and is an adequate complimentary quality control tool that provides a rapid means of classifying food-packaging products based on odors from the print material.

For the Cyranose 320, there is a limitation of ten observations that may be used in a database class and six classes that may be used in a database method. This is due to the fact that it is a hand-held unit that performs the statistical analysis onboard and does not have the advantage of using a powerful external computer. In any event, this limitation provides a significant handicap when attempting to build a database using assorted products as it is not possible to use many observations. Subsequently, the ten observations used to build each of the assorted 'conforming' and 'non-conforming' classes were taken randomly from the available assorted films. The PCNose software was used to analyze the results and to classify unknowns. Figure 14 shows the obtained CDA plot where it can be visually seen from this plot that there

clear separation between the 'conforming' and 'non-conforming' classes. The reported percent recognition during cross-validation was 100% indicating that the database was valid and complete separation was achieved. This is further supported by a reported Mahalanobis interclass distance, D, of 9.735 which is greater than the value of 5 required for good separation. SAS was used to gain additional information and its results were again verified for the Cyranose through an identical Mahalanobis value and CDA plot. The CDA method using SAS reported an $F_{Mahalanobis}$ of 98.8 significant with a p-value less than 0.0001. This value is three times higher than that of the FOX 3000 indicating that it achieves better separation than that instrument. The reported Wilks' Lambda was 0.0366 with an F-statistic of 98.8 significant with a p-value less than 0.0001. The model fit therefore is approximately 96%. The most important indication of the system's usefulness again however is the correct classification rate of the unknowns. Table 7 provides the results of the unknowns analyses as performed by PCNose Software. This software uses the minimum Mahalanobis distance to classify unknowns. Table 7 shows that the PCNose software correctly identified 100% of both the unknowns. Also, it is seen that the Mahalanobis distances are all less than 5 to the 'conforming' class and greater than 5 to the 'non-conforming' class. The average Mahalanobis distance to the conforming class was 2.7 for Unknown1 and 1.9 for Unknown2 further confirming the classifications made. From these results, it is concluded that the Cyranose 320 is also suitable for this application, despite its observation limitations, and is an adequate complimentary quality control tool that provides a rapid means of classifying packaging products based on odors from the print material.

For the QMB6, there is no limitation on the number of observations or classes that may be used in a database. Consequently, ten observations used from each available sample to build each of the assorted 'conforming' and 'non-conforming'. A major problem was encountered here however as adequate signals for the two paper-based samples could not be obtained using this system. In fact, negative readings were obtained indicating possible sensor damage. Heptane standards were then tested and compared to older recognition patterns and it was determined that no sensor damage had occurred. Subsequently, the databases were built without those samples and the unknowns were tested.

It should be noted that this problem of obtaining sufficient readings for all samples immediately brings into question the usefulness of this instrument in this application. The QMBSoft software was used to analyze the results and to classify unknowns. Figure 15 shows

the obtained DFA (CDA) plot where it can be visually seen from this plot that there is clear separation between the 'conforming' and 'non-conforming' classes. SAS was used to gain additional information and the results were verified for the QMB6 through a visually identical CDA plot.

The CDA method using SAS reported Mahalanobis interclass distance, $D^2$, of 26.7 and an $F_{Mahalanobis}$ of 54.2 significant with a p-value less than 0.0001. The percent recognition during cross-validation was 100%. This value and the Mahalanobis distance, D, greater than 5 both support the visual conclusions of good separation made from Figure 15. The $F_{Mahalanobis}$ value falls between those found for the Cyranose 320 and the FOX 3000 indicating that the separation of the groups achieved by the QMB6 is worse than the Cyranose 320 and better than the FOX 3000.

The reported Wilks' Lambda was 0.1402 with an F-statistic of 98.8 significant with a p-value less than 0.0001. The model fit therefore is approximately 86%. Yet again, the most important indication of the system's usefulness is the correct classification rate of the unknowns. Table 8 provides the results of the unknown analyses as performed by QMBSoft Software. This software also uses the minimum Mahalanobis distance to classify unknowns as well as a matching coefficient. Table 8 shows that the QMBSoft software correctly identified 100% of both the unknowns. Also, it is seen that the Mahalanobis distances are all less than 5 to the 'conforming' class and greater than 5 to the 'non-conforming' class with the average Mahalanobis distance to the conforming class was 2.37 for Unknown1 and 1.11 for Unknown2 further confirming the classifications made. These values are less than those found using the Cyranose 320 and indicate a stronger classification. The use of more observations per class is the most likely reason for the stronger classification. The average matching coefficients of 73% for Unknown1 and 84% for Unknown2 given by QMBSoft also support the classifications made. From these results, it may only be concluded that the QMB6 is suitable for this application when using polymer film based materials only. Given this limitation, it is an adequate complimentary quality control tool that provides a rapid means of classifying packaging products based on odors from the print material. Most industry professionals would desire an instrument that covers the full range of products.

*Other Factors and Recommendations*

The most prominent factor not yet discussed when comparing these systems is the price. The FOX 3000 with the autosampler is approximately $120,000, the handheld Cyranose 320 is $8,000, and the QMB6 with the autosampler is approximately $60,000. This is a significant difference in price range. However, ultimately it is the desired use of the product that would determine which instrument, if any, should be selected for purchase.

The Cyranose 320, as a hand-held unit, provides an advantage in that it opens the door to a wide variety of applications. Because of its low capital investment costs and its portability, it may be used more closely with sensory evaluation measures. The actual sampling procedure used during sensory analysis may also be used with Cyranose as the analyses may be performed concurrently. Because the Cyranose 320 uses ambient air as the carrier gas, it is not believed that it would achieve adequate results if used on the production floor of a printing facility without first testing the machine in that environment. Such an environment carries levels of volatiles in the air that may be significant to mask the desired signals even if the chemical air filter accessory is used with the Cyranose 320.

The FOX 3000 and QMB6 systems use an autosampler that is more ideal in a laboratory situation. If there are numerous samples to be run, it may be a requirement that the samples are not tested manually as is required by the Cyranose 320 regardless of the speed of analysis.

The accompanying software is also a factor when selecting the proper instrument. For all three systems, adequate statistical analysis information is given for the circumstance where the machine has already been established to be adequate in that application. However, in terms of method development and comparison of machines, each system has the drawback of not providing comprehensive descriptive statistics. Data manipulation regarding class development is most user-friendly in the QMBSoft software although the same software is the least user friendly in compiling raw sensor score data. The PCNose software provides the most information through descriptive statistics although it does not allow unknowns to be reanalyzed using different databases and/or different statistical methods without preparing new unknown samples. The AlphaSoft is probably the most balanced of the three software systems. Each system's software also offers additional statistical methods along with discriminant analysis. Depending on which method most suits the desired application, these methods are useful. The AlphaSoft software offers SIMCA modeling and partial least squares modeling, the PCNose

software also offers the partial least squares method as well as K-means, and KNN (k nearest neighbor) , and the QMB6 offers a Gaussian discriminant function that uses cluster analysis and an Artificial Neural Network.

While electronic nose technology has been increasingly developed over the past few decades and has great potential, the technology is still in its infancy. There is yet to be a completely rounded system that provides sufficient discriminatory power and comprehensive analysis software for a wide range of applications. Therefore, it has been the trend to test electronic nose systems for performance in each new application.

Considering the price and the discriminatory power, the Cyrano Sciences Cyranose 320 would be a most suitable choice for this application. However, this statement should be conditioned with the comment that it may be desirable to first test a wider assortment of films and determine if the results are still adequate. The database limitations of the Cyranose 320, if they did in fact prove to be a problem, may be overcome through structuring the database differently. Multiple databases may be developed depending on sublevels of concentrations, or what printing inks dominate a product, or whether the product is composed of multiple layers, or even based upon the type of adhesive used. There are wide ranges of criteria possibilities that may be used to develop databases that overcome any difficulty arising from a wider assortment of film products.

The most well rounded machine is the AlphaM.O.S. FOX 3000. If a system with an autosampler is desired and initial investment is not the most limiting factor, this instrument is very suitable for this application.

**CONCLUSION**

All three electronic nose instruments were found to have adequate discriminatory power when analyzing three classes of retained solvent levels for a single packaging product. The most powerful instrument in that analysis was the Cyranose 320. In analyzing assorted products and unknowns again all three systems adequately discriminated and correctly identified the unknowns with the noted exception that the QMB6 could not analyze the full assortment of products. This indicates that both the Cyranose 320 and FOX 3000 instruments are suitable for this application as a complimentary analysis tool in quality control of food packaging and selection of the proper instrument is dependent on the needs of the purchaser.

**REFERENCES**

Castle L, Mayo A, Gilbert J. 1989. Migration of plasticizers from printing inks into foods. Food Add and Contam 6(4):437-443.

Gilbert J, Castle L, Jickells SM, Mercer A, Sharman M. 1988. Migration from plastics into foodstuffs under realistic conditions of use. Food Add and Contam 5:513-523.

Hotchkiss JH. 1997. Food-packaging interactions influencing quality and safety. Food Add and Contam 14(6):601-607.

Jolliffe IT. 1986. Principal component analysis. New York: Springer-Verlag. 271 p.

Marcus L. 2001. Mahalanobis Distance http://www.qc.edu/Biology/fac_stf/marcus/multisyl/fourth.htm. Queens College. Posted August 3, 2001.

Nerin C, Cacho J, Gancedo P. 1993. Plasticizers from printing inks in a selection of food packagings and their migration to food. Food Additives and Contaminants 10(4):453-460.

Ozdemir M, Ozen BF, Floros JD. 1999. Safety implications from the migration of packaging components into foods. In Proceeding of the 6th Conference of Food Engineering (Barbosa-Canovas GV, and Lombardo SP, editors) – Am Inst of Chem Eng :449-455.

Perkin-Elmer Corporation. 1999. Operators manual for the chemosensory-system QMB6 / HS40XL. Norwalk, CT. HKR Sensorsystems GmbH.

Robertson G. 1993. Food packaging: principles and practice. New York: Marcel Dekker, Inc. 487 p.

Sharma SK, Mulvaney SJ, Rizvi S. 2000. Packaging of foods. In Chapter 18 of Food process engineering: theory and laboratory experiments. New York: John Wiley & Sons, Inc.

Table 1. Mahalanobis distances and F-values from discriminant analysis of classes 1, 2, and 3 using four independent sensors.

| System (Technology) | Mahalanobis Distance, $D^2$ | | | F-value of M-Distance | | |
|---|---|---|---|---|---|---|
| and Sensors Used | 1-2 | 1-3 | 2-3 | 1-2 | 1-3 | 2-3 |
| FOX 3000 (MOS) S1,S6,S4,S5 | 28.9 | 102.3 | 37.1 | 32.1 | 113.7 | 41.3 |
| Cyranose 320 (CPS) S6,S22,S13,S27 | 320.9 | 780.7 | 532.0 | 356.5 | 867.4 | 591.1 |
| QMB6 (QMB) S2,S3,S4,S5 | 26.2 | 99.9 | 67.7 | 29.1 | 111.0 | 75.2 |

*All F-values were significant at $\alpha$-level of 0.05 with p-values < 0.0001*

Table 2. Wilks' Lambda, F-value, and % correct during cross-validation from discriminant analysis of classes 1, 2, and 3 using four independent sensors.

| System (Technology) and Sensors Used | Wilks' Lambda | F-value for W-L | % Correct in Cross-Validation |
|---|---|---|---|
| FOX 3000 (MOS) S1,S6,S4,S5 | 0.0179 | 38.9 | 96.7 |
| Cyranose 320 (CPS) S6,S22,S13,S27 | 0.0001 | 528.9 | 100.0 |
| QMB6 (QMB) S2,S3,S4,S5 | 0.0095 | 55.6 | 96.7 |

*All F-values were significant at $\alpha$-level of 0.05 with p-values < 0.0001*

Table 3. Results of principal component analysis performed using full sensor array

| System | Principal Component | Eigenvalue | Cumulative Proportion of Variation |
|---|---|---|---|
| MOS (12 sensors) | 1 | 11.110 | 0.9258 |
| MOS (12 sensors) | 2 | 0.811 | 0.9934 |
| MOS (12 sensors) | 3 | 0.073 | 0.9995 |
| MOS (12 sensors) | 4 | 0.005 | 0.9999 |
| MOS (12 sensors) | 5 | 0.000 | 1.0000 |
| CPS (32 sensors) | 1 | 29.451 | 0.9203 |
| CPS (32 sensors) | 2 | 2.070 | 0.9850 |
| CPS (32 sensors) | 3 | 0.291 | 0.9941 |
| CPS (32 sensors) | 4 | 0.070 | 0.9963 |
| CPS (32 sensors) | 5 | 0.048 | 0.9978 |
| QMB (6 sensors) | 1 | 5.363 | 0.8938 |
| QMB (6 sensors) | 2 | 0.405 | 0.9613 |
| QMB (6 sensors) | 3 | 0.206 | 0.9957 |
| QMB (6 sensors) | 4 | 0.021 | 0.9992 |
| QMB (6 sensors) | 5 | 0.004 | 0.9999 |

Table 4. Mahalanobis distances and F-values from discriminant analysis of classes 1, 2, and 3 using the first four principal components.

| System | Mahalanobis Distance, $D^2$ | | | F-value of M-Distance | | |
|---|---|---|---|---|---|---|
| | 1-2 | 1-3 | 2-3 | 1-2 | 1-3 | 2-3 |
| FOX 3000 (MOS) | 70.3 | 152.0 | 25.9 | 78.1 | 168.9 | 28.7 |
| Cyranose 320 (CPS) | 229.6 | 579.3 | 206.1 | 252.0 | 576.7 | 207.4 |
| QMB6 (QMB) | 27.1 | 59.4 | 45.8 | 30.1 | 66.0 | 50.9 |

*All F-values were significant at $\alpha$-level of 0.05 with p-values < 0.0001*

Table 5. Wilks' Lambda, F-value, and % correct during cross-validation from discriminant analysis of classes 1, 2, and 3 using the first four principal components.

| System | Wilks' Lambda | F-value for W-L | % Correct in Cross-Validation |
|---|---|---|---|
| FOX 3000 (MOS) | 0.0126 | 47.4 | 100.0 |
| Cyranose 320 (CPS) | 0.0005 | 265.2 | 100.0 |
| QMB6 (QMB) | 0.0139 | 44.9 | 96.7 |

*All F-values were significant at $\alpha$-level of 0.05 with p-values < 0.0001*

Table 6. Results of unknown identifications using the FOX 3000.

| | Unknown1 | | Unknown2 | |
|---|---|---|---|---|
| Sample No. | Recognized Class | % Recognition | Recognized Class | % Recognition |
| 1 | Conforming | 100.0 | Conforming | 100.0 |
| 2 | Conforming | 87.6 | Conforming | 100.0 |
| 3 | Conforming | 94.7 | Conforming | 72.6 |
| 4 | Conforming | 89.0 | Conforming | 71.3 |
| 5 | Conforming | 97.7 | Conforming* | 57.3* |
| 6 | Conforming | 73.6 | Conforming | 100.0 |
| 7 | Conforming | 73.9 | Conforming | 100.0 |
| 8 | Conforming | 87.4 | Conforming | 100.0 |
| 9 | Conforming | 93.0 | Conforming | 100.0 |
| 10 | Conforming | 74.2 | Conforming | 100.0 |
| Average | | 87.11 | | 93.77 |

** According to AlphaSOFT v. 7.01 % recognition value not sufficient to be considered recognized, although the closest class is listed.*

Table 7. Results of unknown identifications using the Cyranose 320.

| | Unknown1 | | Unknown2 | |
|---|---|---|---|---|
| | Mahalanobis (D) | | Mahalanobis (D) | |
| Sample No. | To Conforming Class | To Non-Conforming Class | To Conforming Class | To Non-Conforming Class |
| 1 | 2.1 | 7.5 | 2.0 | 11.8 |
| 2 | 2.5 | 7.1 | 1.9 | 11.8 |
| 3 | 3.5 | 6.2 | 2.0 | 11.9 |
| 4 | 2.7 | 7.0 | 1.5 | 11.3 |
| 5 | 0.9 | 8.9 | 2.1 | 12.0 |
| 6 | 3.2 | 6.4 | 2.4 | 12.1 |
| 7 | 1.2 | 8.3 | 2.0 | 11.8 |
| 8 | 4.0 | 5.6 | 1.5 | 11.2 |
| 9 | 3.3 | 6.3 | 1.5 | 11.0 |
| 10 | 3.8 | 6.0 | 2.0 | 11.8 |
| Average | 2.7 | 6.9 | 1.9 | 11.7 |

Table 8. Results of unknown identifications using the QMB6.

| Sample No. | Unknown1 | | | | Unknown2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Mahalanobis (D) | | Matching Coefficient | | Mahalanobis (D) | | Matching Coefficient | |
| | To Conf Class | To NonConf Class | To Conf Class | To NonConf Class | To Conf Class | To NonConf Class | To Conf Class | To NonConf Class |
| 1 | 3.83 | 6.77 | 69.42 | 30.57 | 2.23 | 6.77 | 75.16 | 24.83 |
| 2 | 3.34 | 6.35 | 72.22 | 27.77 | 1.70 | 6.35 | 78.87 | 21.12 |
| 3 | 1.86 | 6.23 | 78.80 | 21.19 | 1.44 | 6.23 | 81.20 | 18.79 |
| 4 | 2.21 | 5.93 | 74.85 | 25.14 | 1.15 | 5.93 | 83.66 | 16.33 |
| 5 | 1.70 | 5.93 | 74.74 | 25.25 | 1.06 | 5.93 | 84.74 | 15.25 |
| 6 | 2.11 | 5.80 | 72.90 | 27.09 | 0.86 | 5.80 | 87.09 | 12.90 |
| 7 | 2.22 | 5.77 | 72.44 | 27.55 | 0.66 | 5.77 | 89.68 | 10.31 |
| 8 | 2.07 | 5.78 | 72.67 | 27.32 | 0.64 | 5.78 | 90.01 | 9.98 |
| 9 | 2.19 | 5.77 | 71.29 | 28.70 | 0.62 | 5.77 | 90.18 | 9.81 |
| 10 | 2.21 | 5.78 | 69.84 | 30.15 | 0.70 | 5.78 | 89.19 | 10.80 |
| Avg | 2.37 | 6.01 | 72.92 | 27.01 | 1.11 | 6.01 | 84.98 | 15.01 |

Figure Captions

Figure 1. AlphaM.O.S. FOX 3000 workstation. 1) AlphaM.O.S. FOX 3000, 2) HS-50 automated headspace sampler, 3) Nitrogen carrier gas, 4) Controlling computer.

Figure 2. Cyrano Sciences Cyranose 320 workstation. 1) Cyranose 320, 2) Sample heating block, 3) Controlling computer.

Figure 3. HKR Sensorsystems QMB6 workstation. 1) QMB6 Sensor Chamber, 2) HS40 automated headspace sampler, 3) External heat exchanger, 4) External chilling unit, 5) Nitrogen carrier gas, 6) Controlling computer.

Figure 4. CDA projection plot of classes 1, 2, and 3 using 4 metal-oxide semiconducting (MOS) sensors. The four sensors used are sensors 1, 4, 5, and 6 from the FOX 3000.

Figure 5. CDA projection plot of classes 1, 2, and 3 using 4 conducting polymer-composite sensors (CPS). The four sensors used are sensors 6, 13, 22, and 27, from the Cyranose 320.

Figure 6. CDA projection plot of classes 1, 2, and 3 using 4 quartz microbalance sensors (QMB). The four sensors used are sensors 2, 3, 4, and 5, from the QMB6.

Figure 7. DFA (CDA) projection plot using AlphaSoft v.7.01 of classes 1, 2, and 3 from discriminant analysis of all 12 metal-oxide semiconducting (MOS) sensors of the Alpha MOS FOX 3000 system.

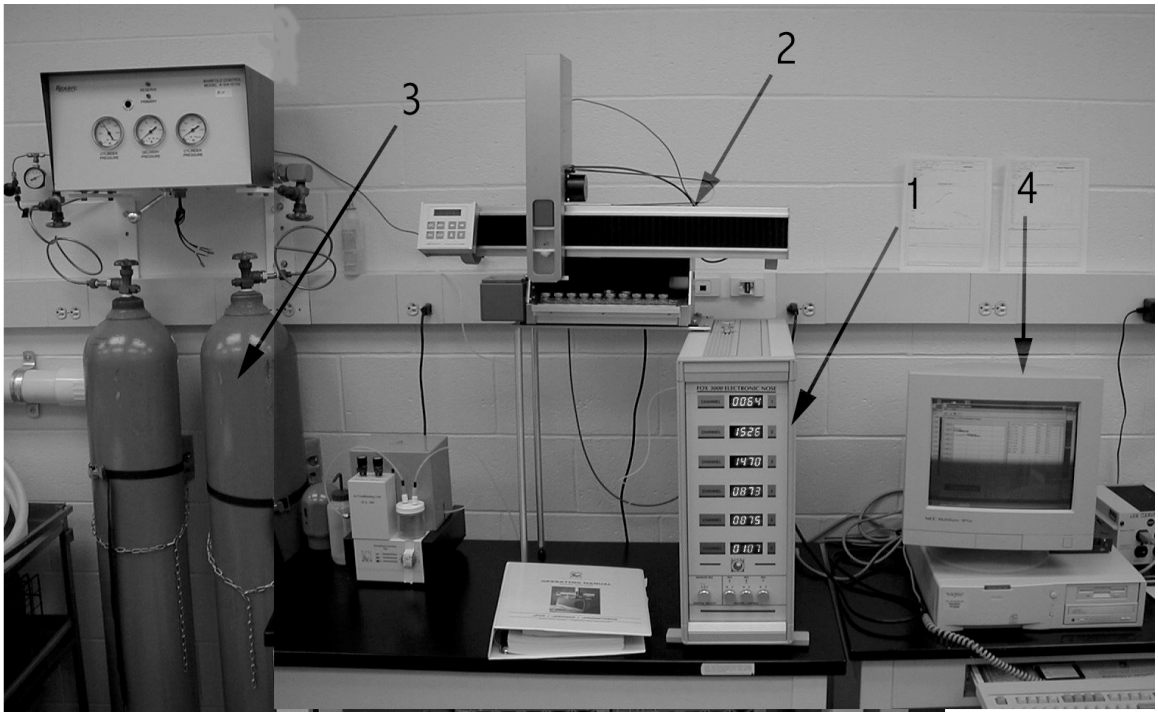
Figure 8. CDA projection plot of using Cyrano Sciences Host Recognition software classes 1, 2, and 3 from the discriminant analysis of the first four principal components derived from all 32 conducting polymer-composite (CPS) sensors of the Cyrano Sciences Cyranose 320 system.

Figure 9. DFA (CDA) projection plot using QMBSoft of classes 1, 2, and 3 from the discriminant analysis of all 6 quartz microbalance (QMB) sensors of the HKR Sensorsystems QMB6 system.

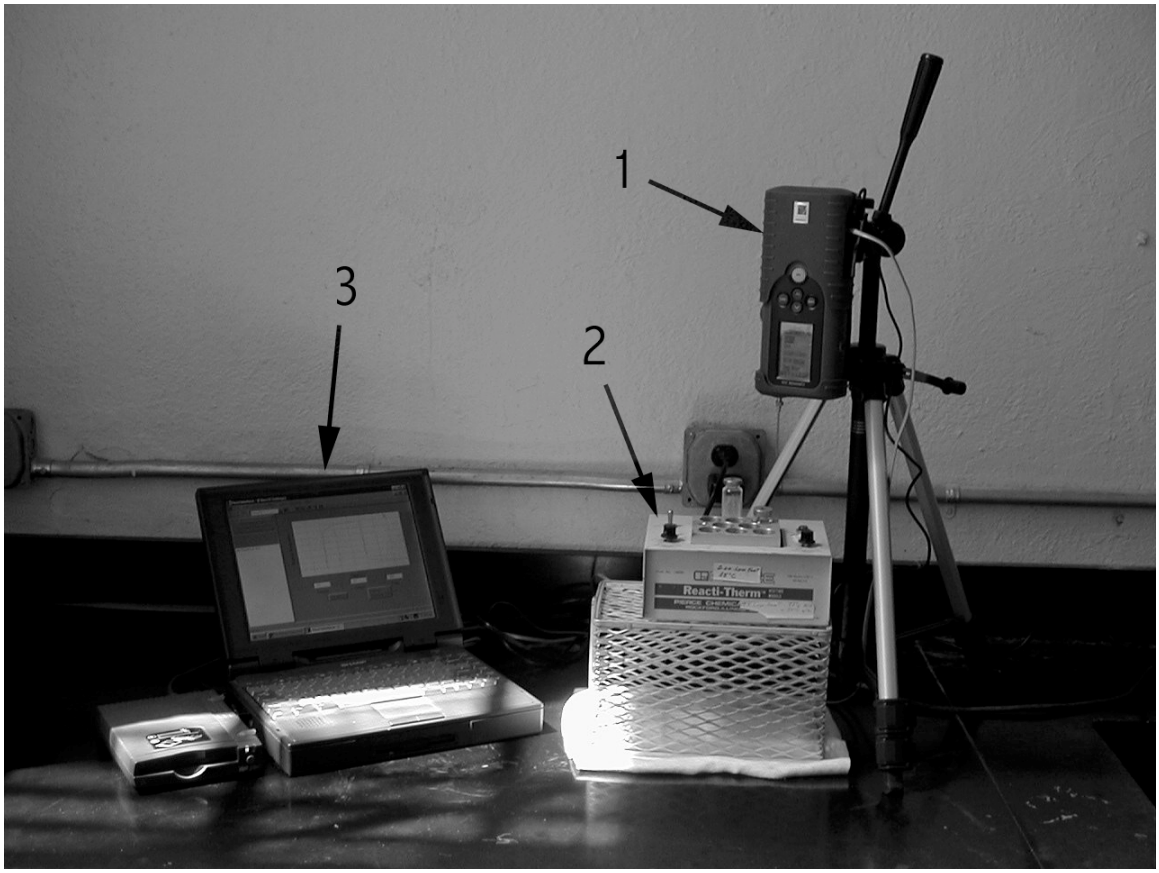
Figure 10. CDA projection plot using SAS of classes 1, 2, and 3 from the discriminant analysis of the first four principal components derived from all twelve metal-oxide semiconducting (MOS) sensors of the Alpha MOS FOX 3000 system.

Figure 11. CDA projection plot using SAS of classes 1, 2, and 3 from the discriminant analysis of the first four principal components derived from all 32 conducting polymer-composite (CPS) sensors of the Cyrano Sciences Cyranose 320 system.

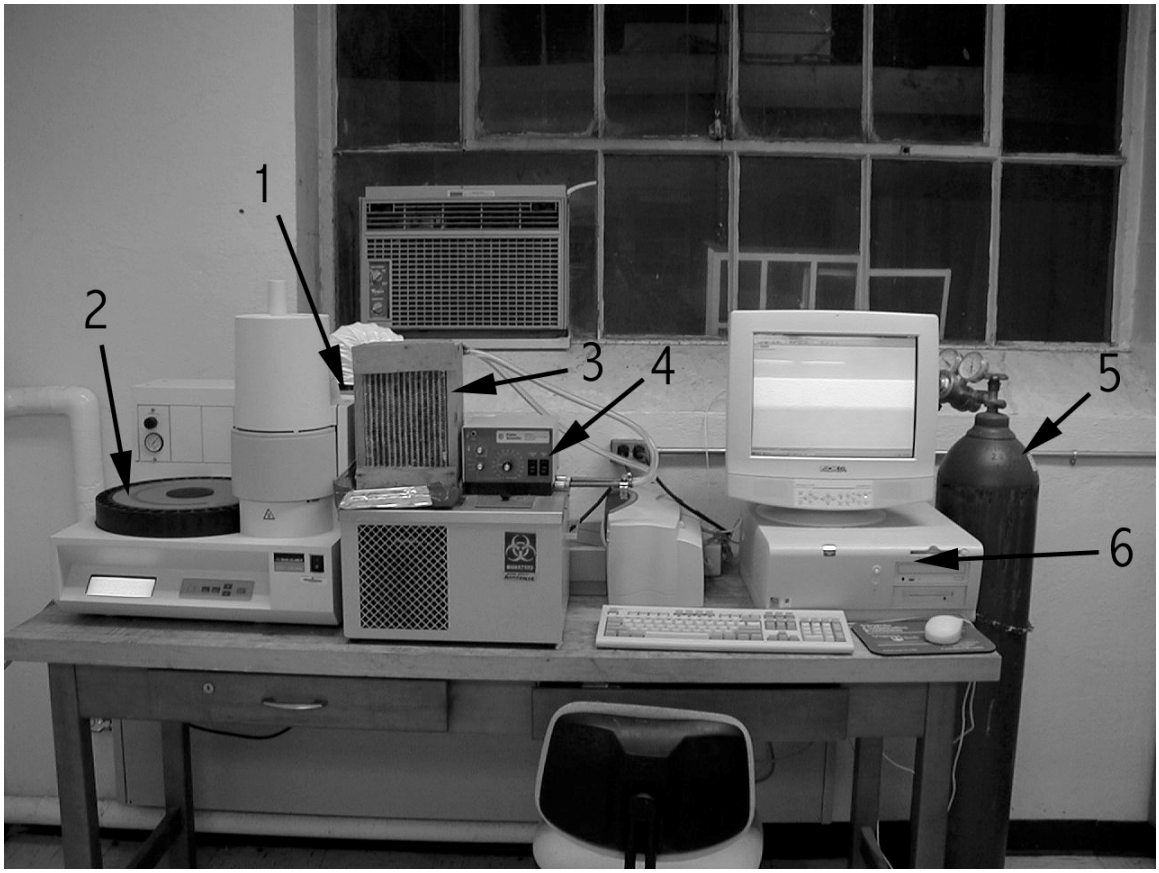
Figure 12. CDA projection plot using SAS of classes 1, 2, and 3 from the discriminant analysis of the first four principal components derived from all six quartz microbalance (QMB) sensors of the HKR Sensorsystems QMB6 system.
Figure 13. CDA plot using AlphaSoft of ‘conforming’ and ‘non-conforming’ classes of assorted films of the Alpha MOS FOX 3000 database.
Figure 14. CDA plot using Host Recognition software of ‘conforming’ and ‘non-conforming’ classes of assorted films of the Cyranose 320 database.
Figure 15. CDA plot using QMBSoft of ‘conforming’ and ‘non-conforming’ classes of assorted films of the QMB6 database.



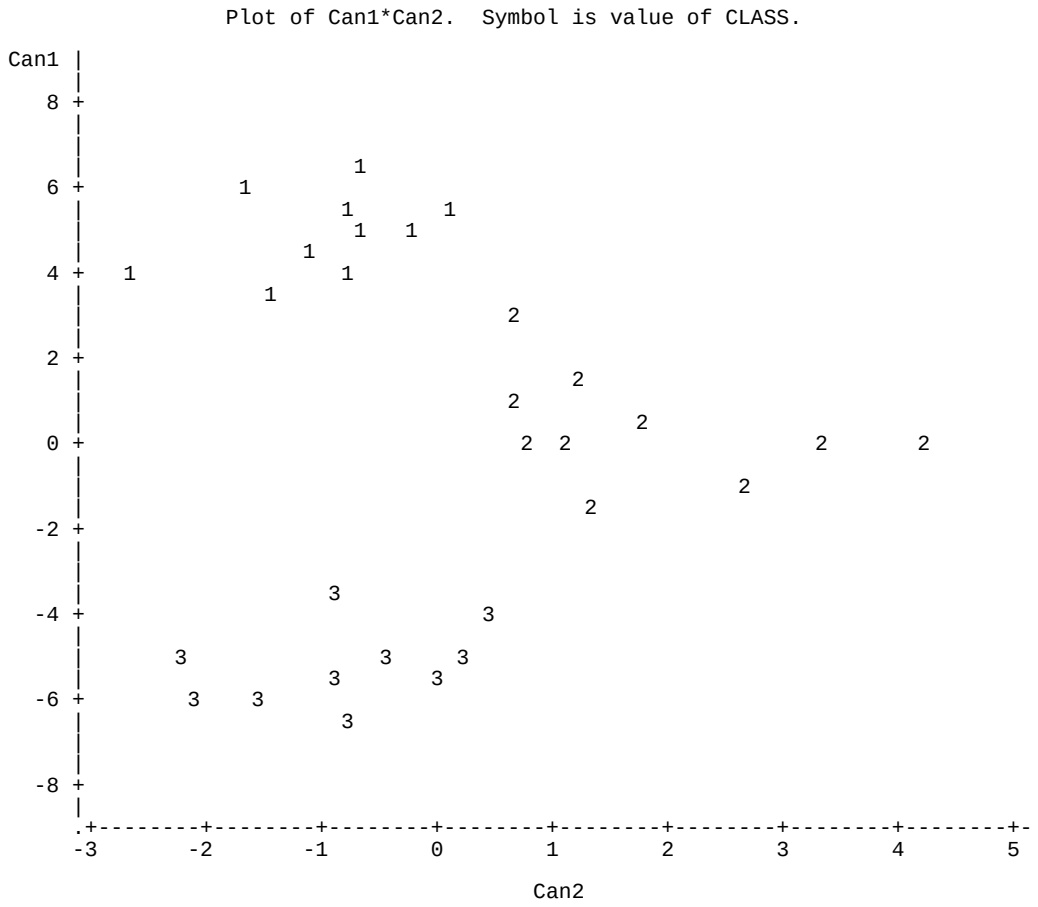

1



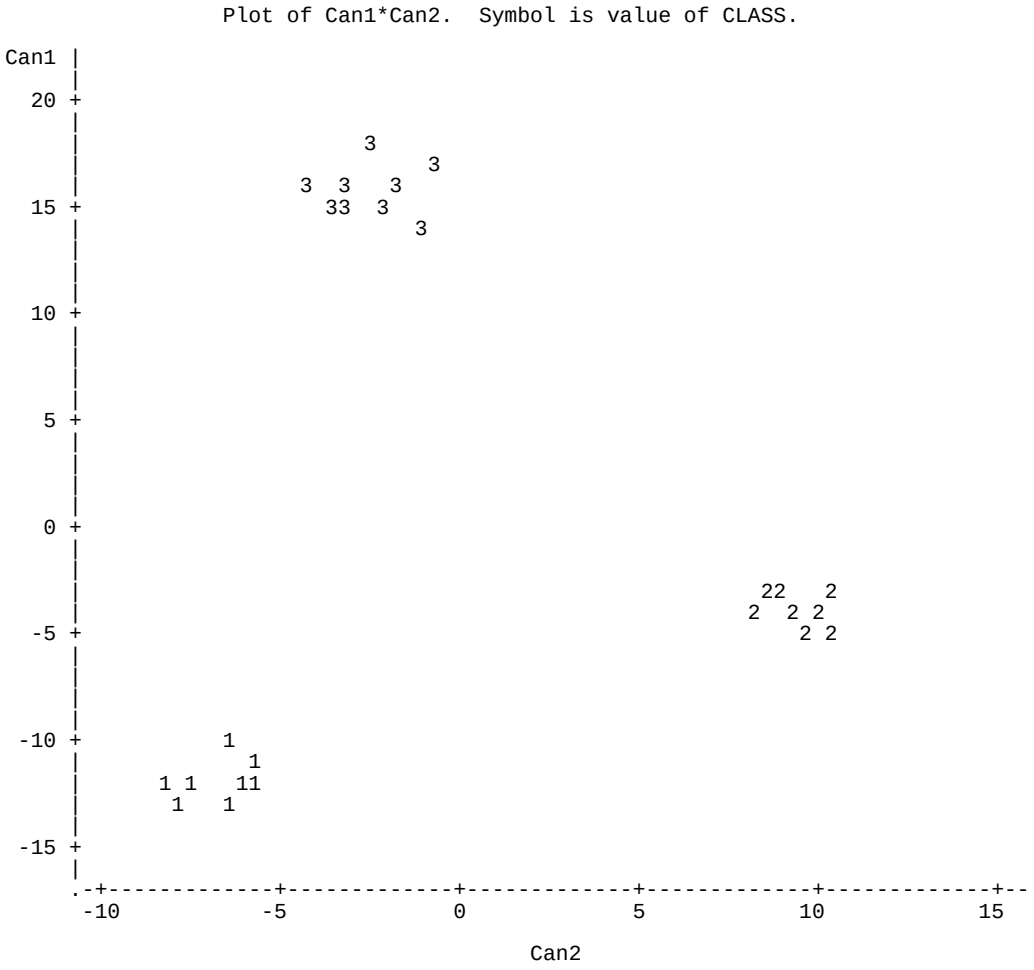

2




3

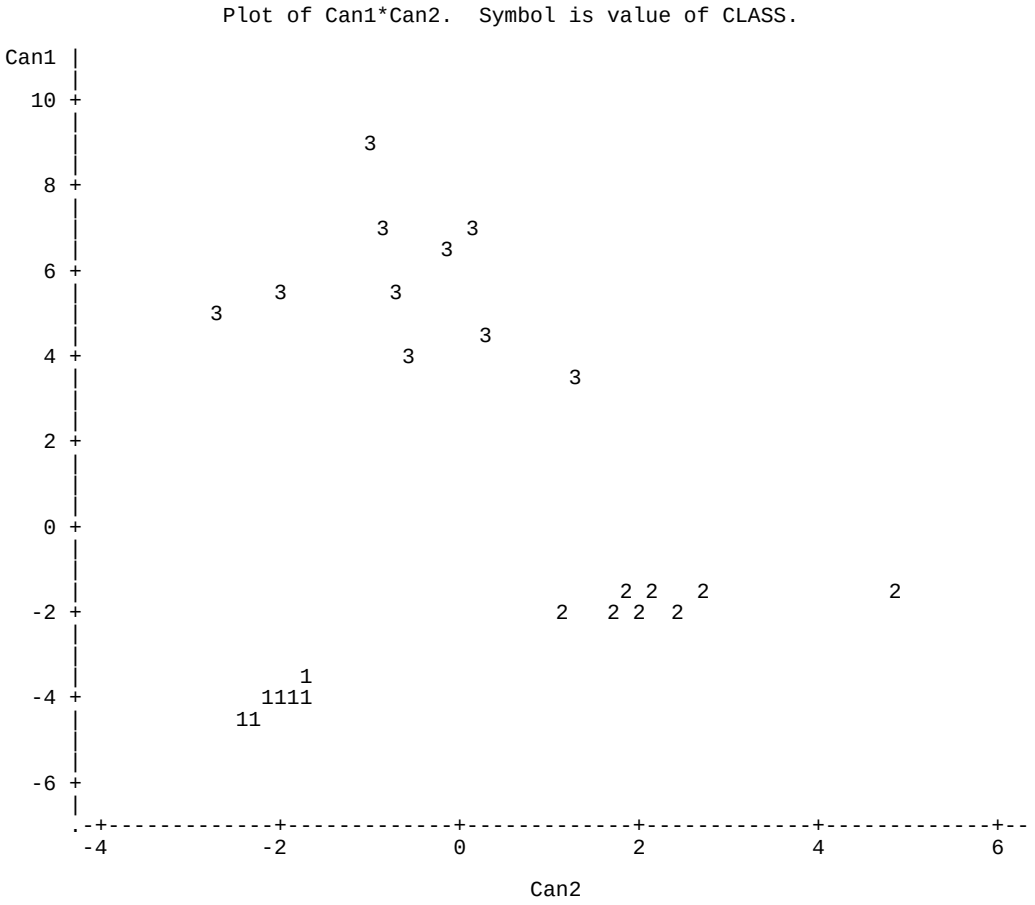



4



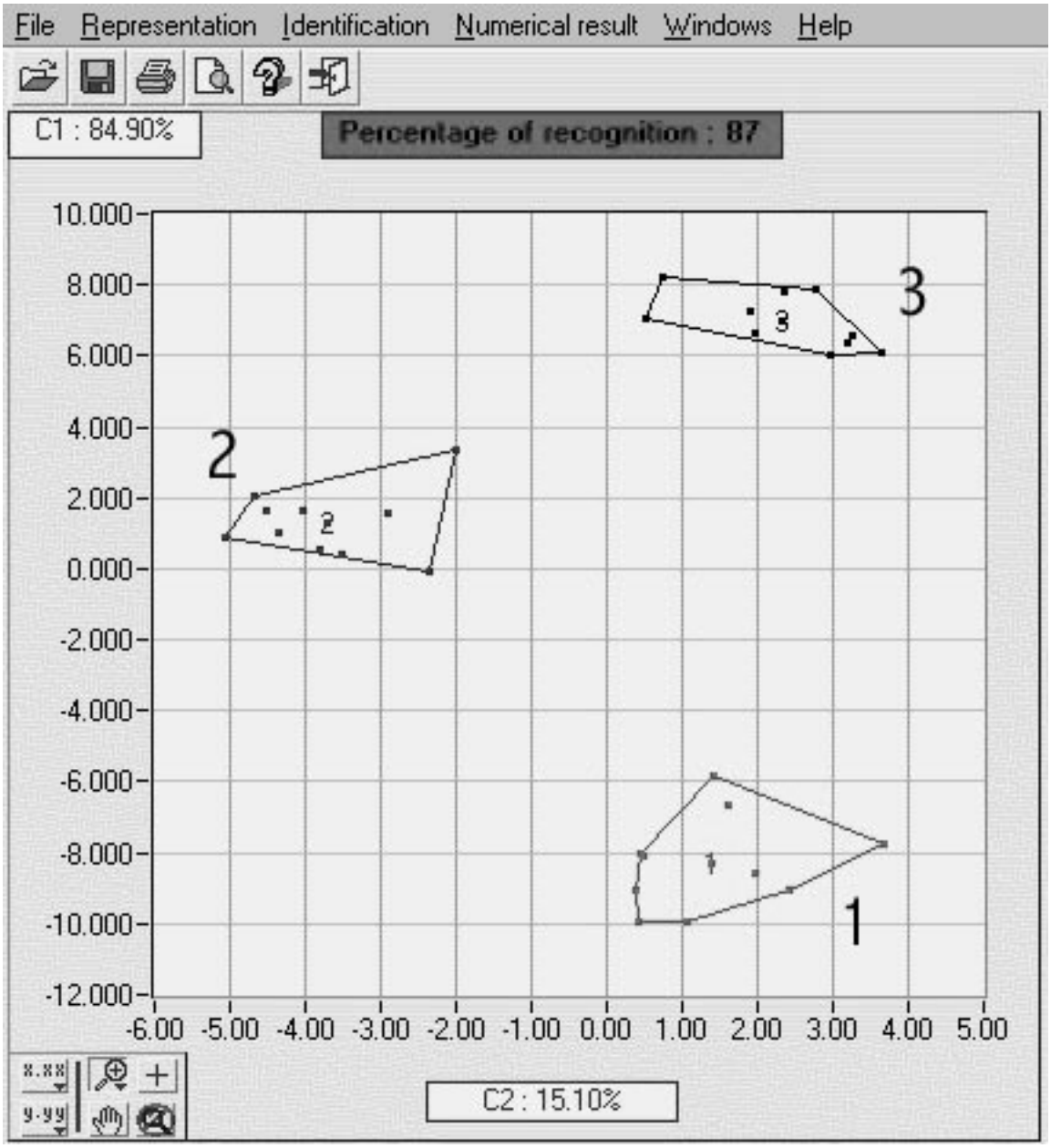

NOTE: 5 obs hidden.

5

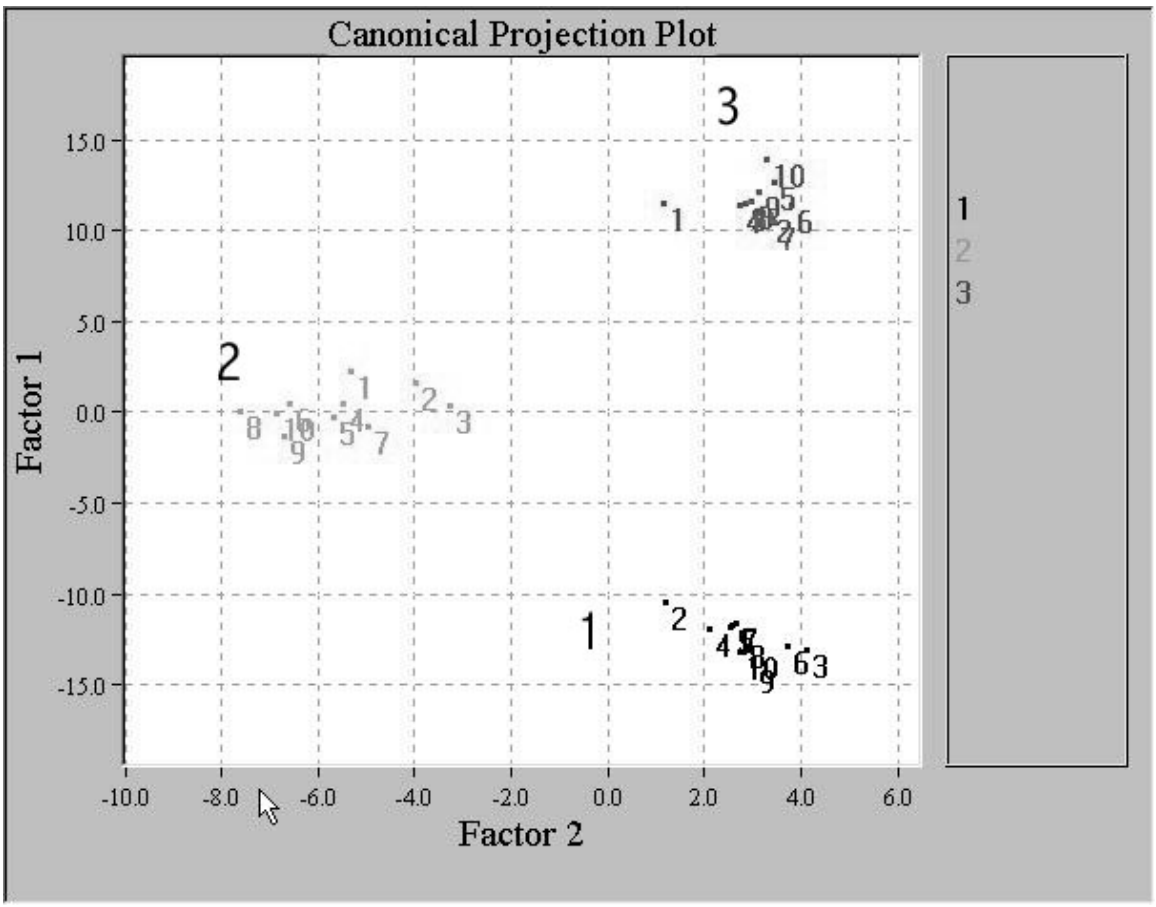



NOTE: 5 obs hidden.

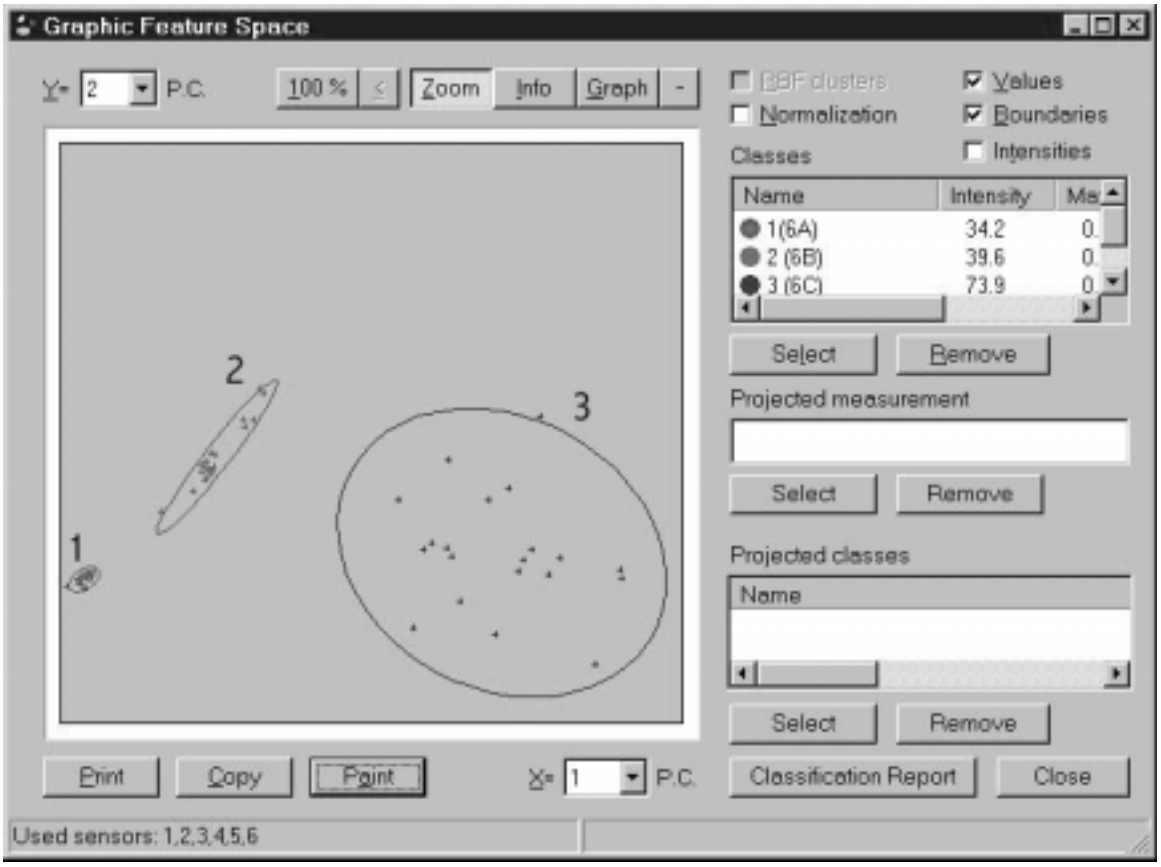
6


File Representation Identification Numerical result Windows Help
C1 : 84.90%
Percentage of recognition : 87
10.000
8.000
6.000
4.000
2.000
0.000
-2.000
-4.000
-6.000
-8.000
-10.000
-12.000
-6.00 -5.00 -4.00 -3.00 -2.00 -1.00 0.00 1.00 2.00 3.00 4.00 5.00
2
3
1
C2 : 15.10%

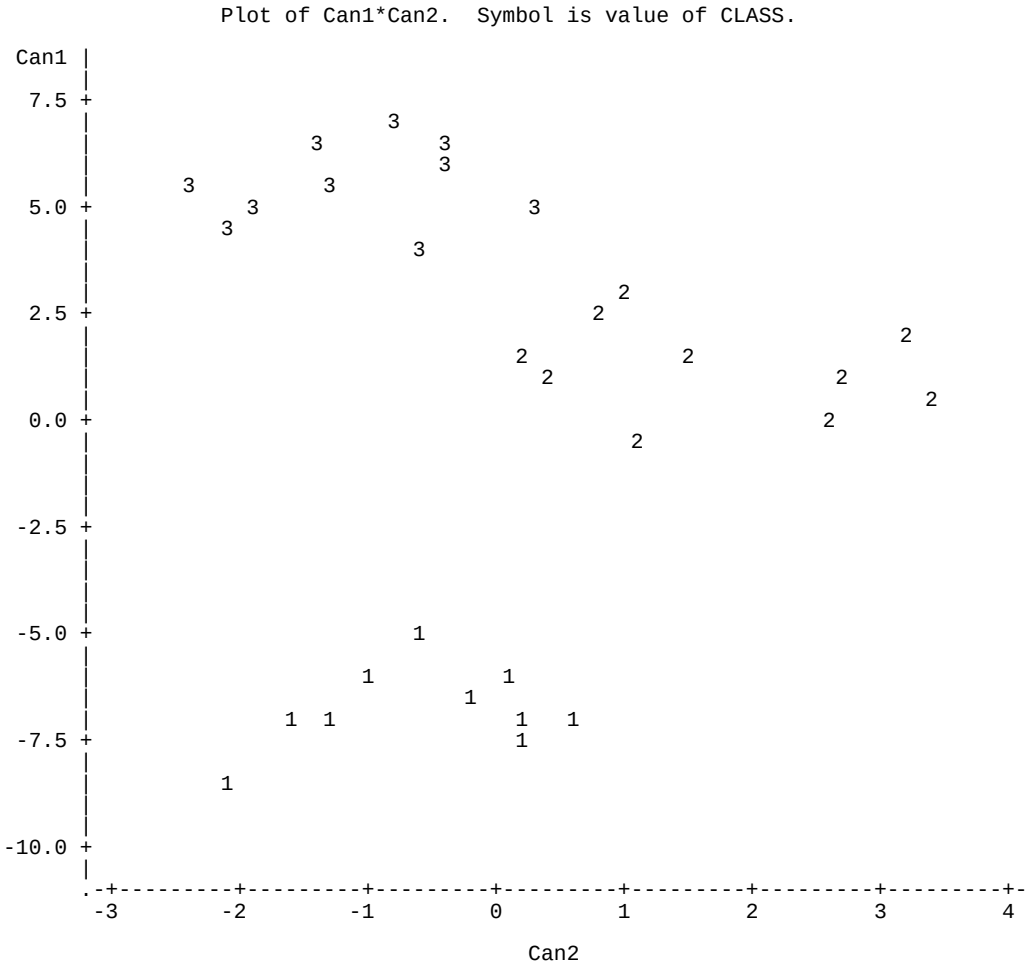
7


Canonical Projection Plot
Factor 1
Factor 2
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-10.0
-8.0
-6.0
-4.0
-2.0
0.0
2.0
4.0
6.0
1
2
3

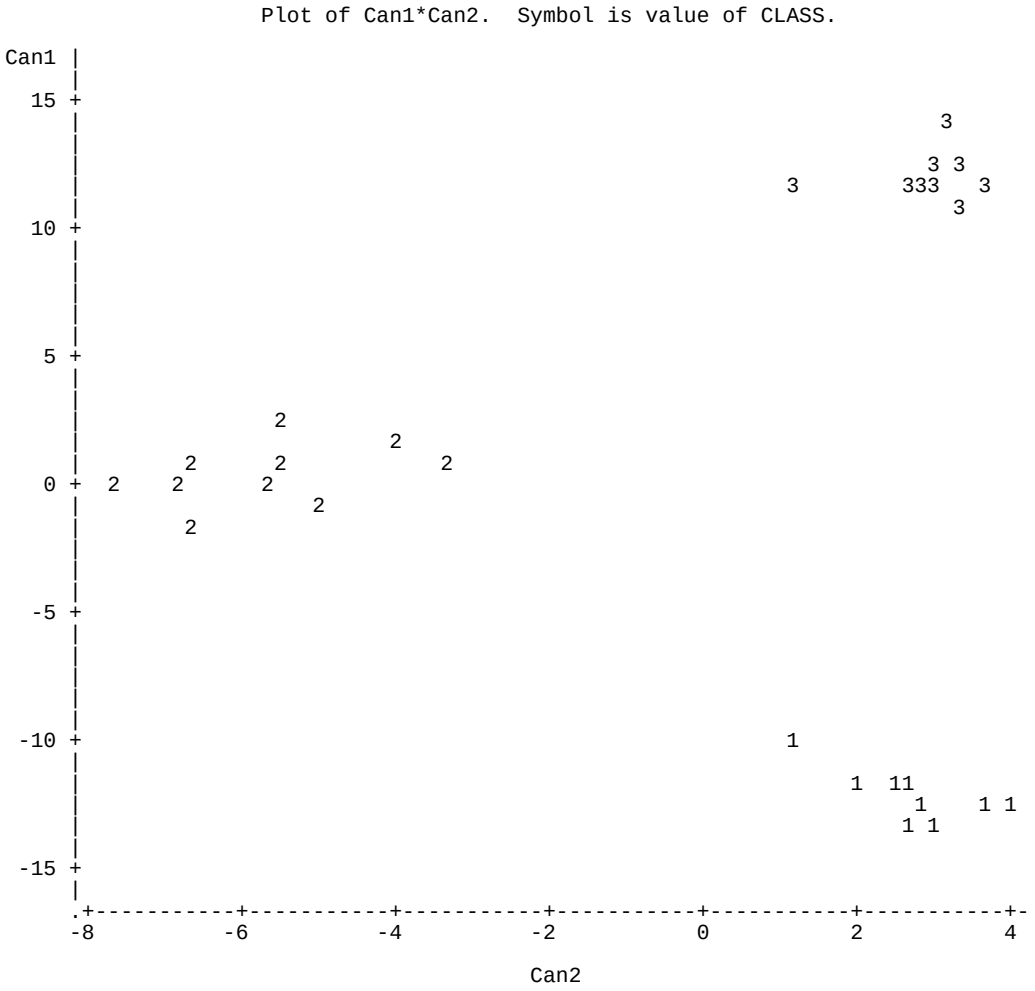
8


Graphic Feature Space
Y= 2 P.C.
100 %
Zoom
Info
Graph
BBF clusters
Normalization
Values
Boundaries
Intensities
Classes
Name
Intensity
1(6A) 34.2
2 (6B) 39.6
3 (6C) 73.9
Select
Remove
Projected measurement
Select
Remove
Projected classes
Name
Select
Remove
1
2
3
Print
Copy
Paint
X= 1 P.C.
Classification Report
Close
Used sensors: 1,2,3,4,5,6

9

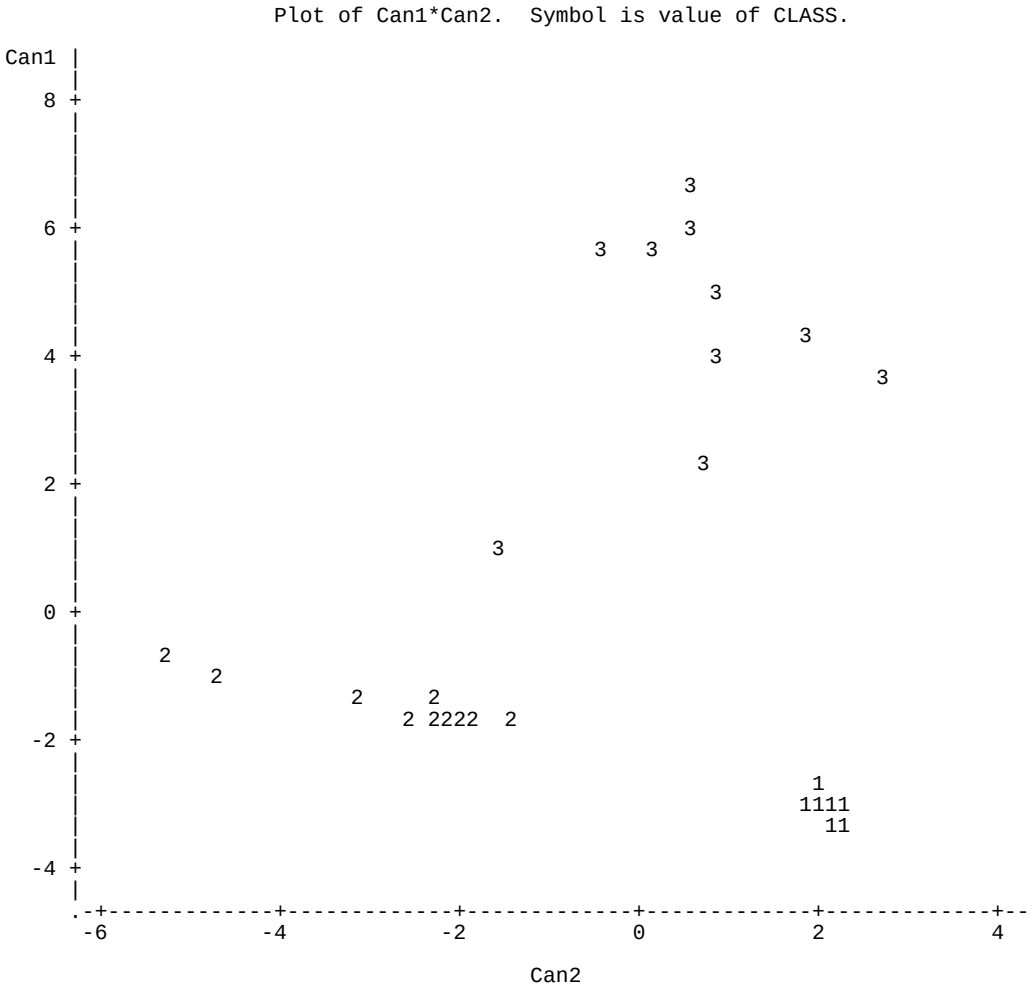

Plot of Can1*Can2. Symbol is value of CLASS.
Can1
7.5
5.0
2.5
0.0
-2.5
-5.0
-7.5
-10.0
-3
-2
-1
0
1
2
3
4
Can2

10



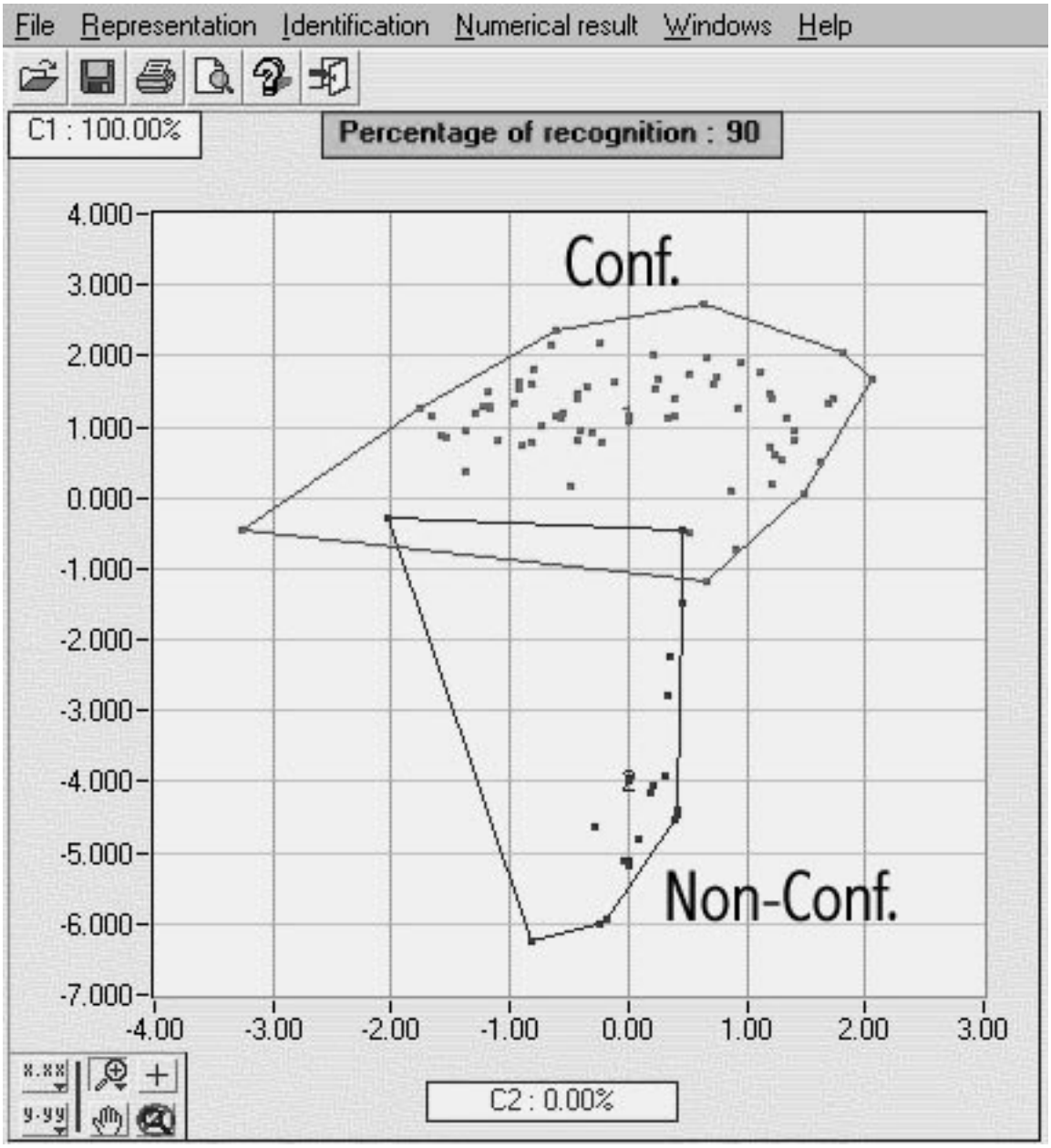

NOTE: 2 obs hidden.

11

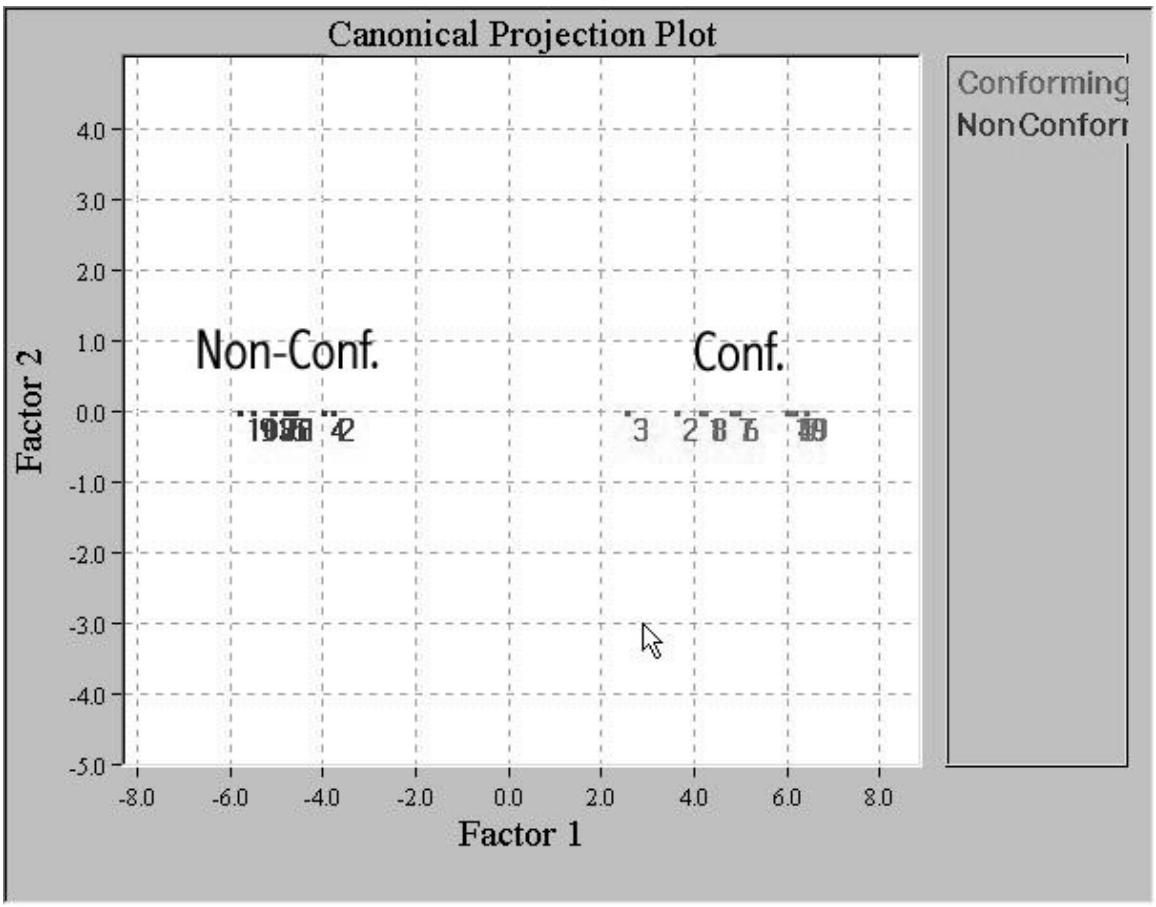



NOTE: 3 obs hidden.

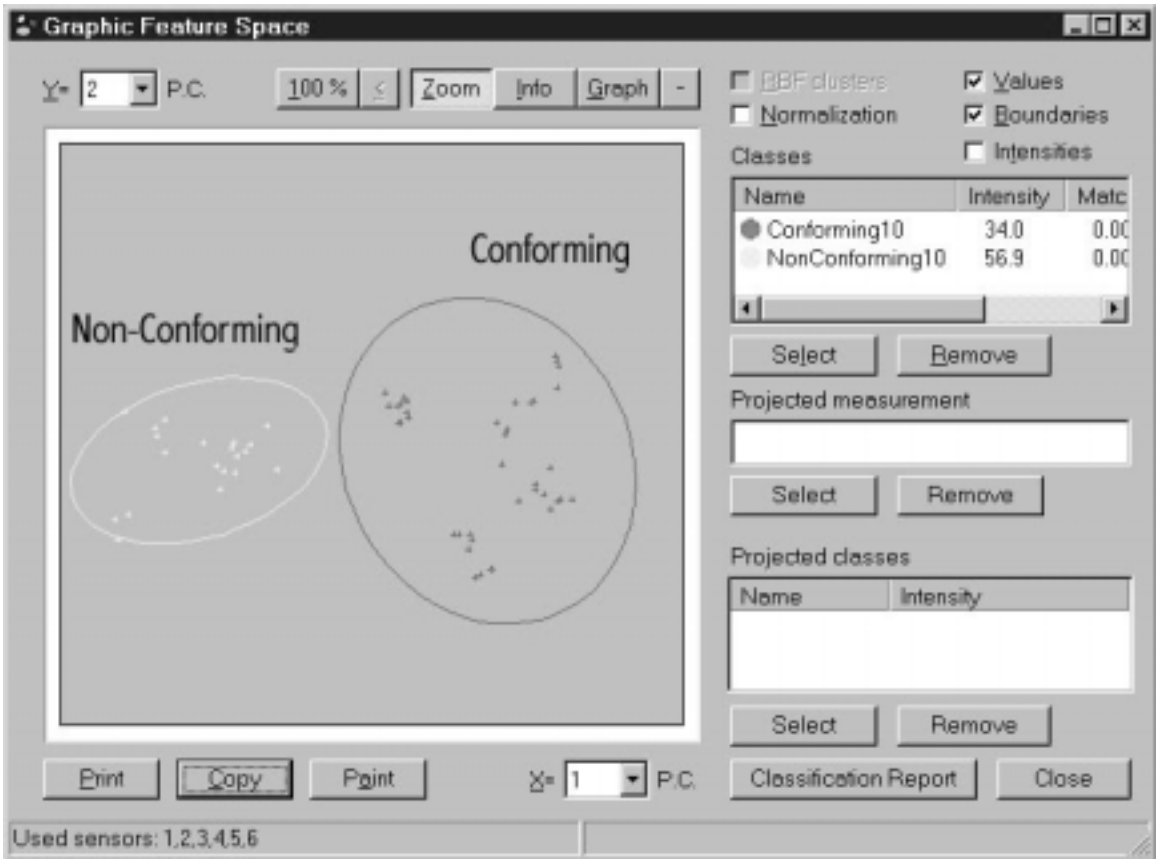
12


File Representation Identification Numerical result Windows Help
C1 : 100.00%
Percentage of recognition : 90
Conf.
Non-Conf.
4.000
3.000
2.000
1.000
0.000
-1.000
-2.000
-3.000
-4.000
-5.000
-6.000
-7.000
-4.00
-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
C2 : 0.00%

13


Canonical Projection Plot
Conforming
NonConforı
Non-Conf.
Conf.
Factor 2
Factor 1
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-8.0
-6.0
-4.0
-2.0
0.0
2.0
4.0
6.0
8.0

14


Graphic Feature Space
Y= 2 P.C.
100 %
Zoom
Info
Graph
RBF clusters
Normalization
Values
Boundaries
Intensities
Classes
Name
Intensity
Matc
Conforming10
34.0
0.0
NonConforming10
56.9
0.0
Select
Remove
Projected measurement
Select
Remove
Projected classes
Name
Intensity
Select
Remove
Conforming
Non-Conforming
Print
Copy
Point
X= 1 P.C.
Classification Report
Close
Used sensors: 1,2,3,4,5,6

15

**Future Work Recommendations**

1. The analyses work should be repeated using more samples. It would also be more ideal to test five or more retained solvent levels of one product. Also, at least one 'non-conforming' product should be used in the unknowns and more unknowns should be tested.
2. It would also be useful to develop an effective 'spiking' method so that the difficulty in obtaining 'non-conforming' samples could be overcome and a fully comprehensive database be built for 'non-conforming' samples.
3. This research involved using analytical gas chromatography techniques to validate or pre-classify the samples used. It would be also very beneficial to use the electronic nose instruments in close conjunction with sensory analysis.
4. Another aspect of the research that may be expanded is the investigation of new machines. Of particular interest may be hybrid sensor array instruments such as the Applied Sensor VOCmeter (eight QMB, four MOS), online versus at-line instruments such as the VOCmeter-V and the AlphaM.O.S. Centauri OVA (six MOS), as well as other handheld units such as the Applied Sensor VOCChek (four QMB).

## VITA

The author, David Van Deventer, was born June 1, 1977 in Syosset, New York. He graduated with a Bachelor of Science degree in Biological Systems Engineering from Virginia Polytechnic Institute and State University in May of 1999. He attained Engineer-in-Training status in May of 1999 and began pursuit of a professional engineering license. He began pursuing a Master of Science degree in Biological Systems Engineering at Virginia Polytechnic Institute and State University in August of 1999.