This is to certify that the
thesis entitled

DEVELOPMENT OF ELECTRONIC NOSE METHOD FOR
EVALUATION OF RESIDUAL SOLVENTS IN LOW DENSITY
POLYETHYLENE

presented by

ISINAY EBRU YUZAY

has been accepted towards fulfillment
of the requirements for the

M.S. degree in School of Packaging

Susan Selke
Major Professor's Signature

Dec. 8, 2004
Date

DEVELOPMENT OF ELECTRONIC NOSE METHOD FOR EVALUATION OF RESIDUAL SOLVENTS IN LOW DENSITY POLYETHYLENE

By

Isinay Ebru Yuzay

A THESIS

Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

2004

ABSTRACT

DEVELOPMENT OF ELECTRONIC NOSE METHOD FOR EVALUATION OF RESIDUAL SOLVENTS IN LOW DENSITY POLYETHYLENE

By

Isinay Ebru Yuzay

High levels of residual volatile organic compounds (VOCs) in packaging films can be a threat to the quality of food products. Currently, a wide range of techniques are available for assessing the residual VOCs in packaging films. An electronic nose (e-nose) system appears to be a viable alternative to traditional techniques, providing simplicity and objectivity. In this study, an objective method has been developed for assessing the residual VOCs from low density polyethylene films. Three VOCs, ethyl acetate, ethyl alcohol, and toluene, were chosen as model solvents. An Alpha Mos Fox 3000 e-nose system was used for qualitative and quantitative analysis of residual solvents. Once the optimum e-nose parameters were determined for all of the model solvent samples, the measurements were made for single and binary solvent mixtures. The responses obtained from the e-nose were processed with multivariate statistical analysis methods (PCA, DFA, and PLS) and compared with gas chromatography, which is currently used for determining the amounts of residual VOCs in packaging films. The results indicated that there was good agreement between the e-nose responses and gas chromatography results. Both single and binary solvent mixture concentrations were successfully predicted with the proposed method.

DEDICATION

This thesis is dedicated to my parents, Sevgi and Fuat Yuzay, and my brother Atalay Yuzay, whose hearts and prayers were always with me during my education

ACKNOWLEDGMENTS

Over the past two years, I have had lots of encouragement, words of wisdom, and gracious contributions from many people that made this research possible. But some of these people deserve special mentioning.

I would like to thank my major advisor, Dr. Susan Selke for her deep insight and guidance. I would also like to thank my committee members, Dr Bruce Harte and Dr. Janice Harte for their support and encouragement.

Center for Food and Pharmaceutical Packaging Research (CFPPR) provided partial support funding for this project. This support is greatly acknowledged.

A special note of recognition goes to Hsin-Yen Chung not only for being the best lab-mate with whom I had stimulating scientific discussions, but also for patiently helping me when an e-nose and computers were not friendly to me.

Finally, I sincerely express my appreciation to my parents and brother for their love, support, and reassurance throughout this challenging endeavor. I do not think words can be ever enough to express my gratitude to them. Thanks.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Quality control of packaging films can be considered as a critical issue in the food industry due to the possibility of migration of substances from packaging films into food products (Robertson, 1993). Particularly, the volatile organic compounds (VOCs) released from printing inks, adhesives, and polymers present in flexible food packaging may give off-odor or taste and significantly alter the quality of food products (Van Deventer and Mallikarjunan, 2002). Therefore, it is highly desirable to have simple and effective quality control methods for qualitatively assessing the volatile compounds as well as to determine the level of residual VOCs in the packaging films. Currently, there are several methods available for analyzing VOCs from plastic packaging film and their printing inks. Gas chromatography (GC), gas chromatography-mass spectroscopy (GC/MS), multiple headspace solid-phase microextraction (HS-SPME) and sensory evaluation are extensively used for this purpose (Robertson, 1993).

The chromatographic techniques are used to provide quantitative and qualitative information about the volatile compounds that are present in packaging films. These techniques allow accurate and objective analysis of volatile compounds. However, they require high levels of expertise and time (Pearce et al., 2003). In recent years, use of gas chromatography has become a standard method of quantifying the level of residual VOCs in packaging film. ASTM F1884, standard test method for determining residual solvents in

packaging films, is used to assess the VOCs from packaging films in the facilities manufacturing packaging materials.

Sensory evaluation can also be an effective tool in terms of qualitative analysis of VOCs in packaging films. Although it requires extensive time to train sensory panelists, well-trained sensory panelists are consistent in their evaluations. On the other hand, untrained (consumer) panelists can be subjective in their evaluations. Hence, obtaining a consistent evaluation can be difficult (Pearce et al., 2003).

While all these techniques can help in the process of assessing and controlling the amount of VOCs in food packaging materials, each technique has its own limitations. Therefore, there is a need for an objective tool that can rapidly provide results for quality control purposes. The electronic nose (e-nose) systems appear to be a viable alternative to traditional techniques, providing operational simplicity for assessing VOCs in packaging films (Suman et al., 2003). The e-nose is capable of detecting/recognizing and discriminating volatiles emitted from liquid or solid samples, using sensor arrays. Moreover, it can predict the amount of volatiles from a large range of materials (Alpha MOS Fox 3000 manual, 2001). To the best of our knowledge, the majority of the literature on the e-nose has been focused on identification of VOCs. But, there are limited amounts of information about quantification of VOCs by using the e-nose. Therefore, of particular interest to us is not only qualitative identification of the residual solvents, but also the prediction of the total amount of residual solvents. Quantification of residual solvents can be very desirable in real life, and

it is much more challenging to predict concentration levels of single solvents or mixtures than qualification of different residual solvents. As a result, in this research, a considerable amount of effort was made to develop a standard method for the quantitative determination of VOCs in low density polyethylene films, that can be extremely advantageous in quality control of packaging materials.

The objectives of this study are:

1. Develop a standard method, by using the e-nose, to assess VOCs from low density polyethylene films.
2. To correlate e-nose results with gas chromatography, which is currently the standard method for determining the amounts of VOCs in packaging film.

It is assumed that the results of this study would enable better and faster quality control of packaging materials, where quality is associated with total amount of residual VOCs, since this new method offers operational simplicity and reproducibility.

2. BACKGROUND AND MOTIVATION

It is well known that the use of plastic films for food packaging may cause off-odor and off-flavor problems which alter the quality of the food product. In most cases, the migration of residual volatile organic compounds (VOCs) from the film into the food is responsible for the off-odor and flavor (Maneesin, 2001; Das, 2003). VOCs can be defined as volatile compounds whose vapor pressure at 20°C (293.15°F) is 0.01 kPa or greater (Wypych, 2001).

The sources of VOCs in plastic films can be classified as follows: solvents in the printing inks; solvents in the lamination adhesives; additives in polymers; possible residuals that form during manufacturing of the films (Ezquerro et al., 2003).

2.1 Residual Solvents from Printing Inks and Adhesives

Printing inks and adhesives composed of solvent-based systems are well known for being a contributor to off-odor and off-flavor. The residual solvent in solvent-based printing inks and adhesives that are used in lamination of packaging films can be absorbed by the food and can impact the taste and aroma of many food products, particularly chocolate, confections, snacks, coffee, and tea (Lin, 1995). Therefore, the packaging film materials are subject to strict quality control requirements. The FDA has issued a guidance which sets limits on the level of VOCs in food contact packaging materials. The European Union also has published regulations on this issue (Robertson, 1993; Williams, 2001; Begley, 1997). Since regulations become more restrictive for the residual

solvents, there is a growing tendency among converters to reduce and control the amounts of VOCs in the printing inks and adhesives.

Most of the flexible packaging material used for food products is printed. During the printing process, the inks and adhesives can be diluted with solvents which are removed by evaporation as the printed substrates are passed through the dryers. Flexography and roto-gravure are the main printing techniques used by converters. It is estimated that about 60% of printed packaging in the USA is printed by the flexographic process and less than 20% is printed by roto-gravure (Savastotano, 2003). Flexography is a relief printing process which is widely used in food packaging due to its high printing speed. In the flexographic printing process, ink is collected from an ink duct by a rubber roller and transferred on an anilox roller, which is made of ceramic and is etched with small cells that collect ink from the rubber roller and deliver it to the photopolymer plates (cliché). A design on the photopolymer plates is put on the printing substrates. Gravure is also used in food packaging. It is an intaglio printing process particularly suited to very long print runs and where very high print quality is required. In the gravure printing process, a design is mechanically engraved onto the surface of a copper cylinder. This cylinder is submerged in ink and then the excess amount of ink on the cylinder is removed by a doctor blade. The ink contained in the engraved cells is transferred from the cylinder to the printing substrate due to the high surface energy of printing materials (Robertson, 2003).

In many cases, solvent-based inks are used for both printing processes. A typical solvent-based ink consists of four essential ingredients. The first is

pigments which provide color. The second is binders whose function is to bind the pigment to the printing surface. The third ingredient is additives which are used for special purposes such as improving adhesion, controlling the viscosity, etc. The forth ingredient is solvents. There are two basic functions of solvents: (1) to dissolve a wide variety of binders such as nitrocellulose, cellulose ethers and esters, polyamides, and acrylics and to carry the pigment and other components to the surface of the substrate, and (2) to cause the drying of the printed ink film (Soroka, 1995). The great majority of solvent-based inks are based on solvent mixtures, usually alcohol, ester, aliphatic and aromatic hydrocarbon and ether mixtures. There seems to be an almost infinite number of solvents possible for formulating printing inks. However, there are several important factors to consider in selecting a suitable combination from among these solvents; boiling range, flash point, evaporation rate, solvency (solvent power), chemical stability, and toxicity (Apps, 1958). In this research, only the effect of evaporation rate was covered.

The evaporation rate is one of the properties of solvents that is vital in printing inks. A wide range of solvent-based printing inks dry by evaporation of solvents. The evaporation rate is a function of the vapor pressure, heat of vaporization at the liquid temperature, the speed of the air stream above the liquid, the thermal conductivity of the air, the area of the surface, and the differences of temperature of the evaporating liquid and the air. The rate of evaporation of the solvents is often given as a numerical value relative to the some other solvent as a standard. There are two solvents which are normally used as standards, diethyl ether and

n-butyl acetate (Apps, 1958: Thompson, 1998). It is interesting to note that for unknown reasons, n-butyl acetate was chosen as the standard in the U.S., but diethyl ether was used in Europe. Table 2.1 gives evaporation rates for some solvents commonly used in flexo and gravure printing inks.

Table 2.1 Evaporation rate for the solvents commonly used in printing inks (Wypych, 2001)

Solvent Name	Evaporation Rate (n-butyl acetate:1.0)
Ethyl acetate	6.2
Butyl acetate	1.0
N-propyl acetate	2.76
Ethyl alcohol	3.2
Isopropyl alcohol	3.0
Acetone	10.0
Methyl ethyl ketone	5.7
Hexane	9.0
Benzene	6.1
N-butanol	0.45
Diethanolamine	0.001
Ethylene glycol	0.004
Water	1.8

In addition, some resins (binders) and pigments used in printing inks are solvent retentive, which can affect the evaporation rate of the solvents. Generally, soft resins are apt to hold the solvents more than hard resins due to their chemical structure (Apps, 1958; Thompson, 2001). A higher solid content in hard binders reduces the amount of solvent that has to be evaporated and therefore increases the drying speed. Conversely, the soft resins, having relatively less solids content, tend to retain solvent. As a result, the printing

solvents that are retained on the packaging film might migrate into food or the headspace of the package and cause off-odor or flavor. Hence, determining/ controlling the amount of residual solvents left in packaging film is of primary interest in the food packaging industry.

2.2 Residual Solvents from the Film Manufacturing Process

VOCs such as hydrocarbons, alcohols, aldehydes, ketones, and carboxylic acids in packaging materials can also be formed by thermo-oxidative degradation of polyolefins during the extrusion coating process. Extrusion parameters such as temperature and speed have an enormous impact on VOC formation (Ezquerro et al., 2003). Therefore, it is necessary to develop an effective method to control the process parameters. Further discussion of this subject is beyond the scope of this research.

2.3 Flexible Packaging Materials

There are a considerable number of different single and multilayer polymer films used as food packaging materials. The polymer of interest in this study is low density polyethylene (LDPE), because it is the most used polymer film in the food industry (Robertson, 1993). LDPE offers the advantages of inertness, good barrier to water, heatsealability, and chemical resistance. However, due to its polyolefinic nature, LDPE tends to retain non-polar compounds (Lopez-Rubio, 2003). Therefore, it is worthwhile to explore the residual solvents in LDPEs.

2.4 Packaging Migration

Packaging migration is important in the food industry since it can change the organoleptic properties of the food. As explained by Van Deventer and Mallikarjunan (2001), the migration of compounds from polymer film is controlled by diffusion. In most cases the molecular transport obeys Fick's laws of diffusion. Fick's first law is $F = - D_p * (dC_p/dx)$. Further, if the diffusion coefficient is independent of concentration, Fick's second law is $dCp/dt = D_p * (d^2C_p/dx^2)$. F is the rate of transport per unit area of the polymer, D_p is the diffusion coefficient of the migrant in the polymer, C_p is the migrant concentration in the polymer, x is the thickness of the film, and t is the elapsed time. There is much information available about packaging migration, but it is beyond the scope of this research.

2.5 Analysis of VOCs from Packaging Materials

There is a vast amount of scientific literature available regarding the use of chromatographic methods (objective) and sensory panels (subjective) in determining the residual solvents in packaging materials.

ASTM F 1884-98, standard test method for determining residual solvents in packaging films, and ASTM F151-86, test method for residual solvents in flexible barrier films, have been developed to determine residual solvent levels. They are used for evaluation of flexible barrier films in the facilities manufacturing packaging materials. These methods are based on gas chromatography. The known amount of specimen is enclosed in a container and heated to vaporize the residual solvents into the headspace. Then, the headspace sample is analyzed

using gas chromatography. The studies of Kolb and Ettre (1997) and Leland et al. (2001) represent up-to date reviews of different GC techniques for determination of residual solvents. For further discussion, these references are recommended.

Another common method used for analyzing the residual solvents in packaging materials is a sniff test (Huber, 2002). About 1000 cm^2 of plastic packaging material is placed into a clean 1 liter glass jar, which is then sealed. After storage for a pre-determined time and temperature, evaluation of odor can be made by sensory evaluation panels. This method is an effective tool in terms of qualitative analysis of VOCs in packaging films. Although it requires extensive time and money to train sensory panelists, well-trained sensory panelists can give precise and consistent results. On the other hand, untrained (consumer) panelists can be subjective in their evaluations since they tend to fatigue. Hence, obtaining a consistent evaluation can be difficult (Pearce et al., 2003). In addition, residual VOCs ,due to their toxicity effects, can pose a threat to sensory panelists.

For these reasons, it is desirable to use an objective and consistent as well as less labor intensive method. An electronic nose (e-nose) which uses special sensors to mimic the human nose has been developed for this purpose. It generates a characteristic fingerprint of an odor which can be compared to data from different samples, batches and mixtures (Alpha MOS Fox 3000 manual, 2001). Most publications deal with e-nose applications to food, cosmetics, and environmental analysis (Schaller, 1998). However, there are a limited number of

publications referring to packaging applications. Benali et al. (1995) found that an e-nose using multiple discriminate analysis could discriminate between cakes wrapped in various qualities of film, although a sensory panel did not find differences. Bohatier et al. (1995) used the e-nose to analyze off odors in polypropylene samples. Polypropylene samples with off odor could easily be distinguished from an undefective one. Van Deventer and Mallikarjunan (2002) compared and optimized three electronic nose systems. The performance analyses showed that based on discriminatory power and practical features, the Fox 3000 and Cyronose 320 were superior. Suman et al. (2003) used an electronic nose for qualifying the residual solvent from a wide range of single layer and laminated substrates. But, the e-nose could not easily discriminate between polyethylene (PE) samples with methoxyproponal and methoxypropyl acetate and reference PE samples.

3. MATERIALS AND METHODS

3.1 Materials

The following items and equipment were used in this study;

A. Film Samples

The packaging material tested during the study was 1.5 mil thick low density polyethylene (LDPE) supplied by Cello-Foil Products, Inc. (Battle Creek, MI). LDPE was selected since it is one of the most often used flexible packaging materials.

B. Solvents

Three volatile organic compounds, ethyl acetate (esters), ethyl alcohol (alcohols), and toluene (aromatic hydrocarbons), representing three different solvent categories, were chosen as models for solvents of interest in flexible food packaging analysis. Ethyl acetate of 99.8% purity, ethyl alcohol of 95% purity, and toluene of 100% purity were obtained from Aldrich Chemical Co. (Milwaukee, WI). These solvents are commonly used in printing ink and adhesive formulations. The typical physical and chemical properties of the representative solvents are shown in Appendix A.

C. Equipment

- The Fox 3000 electronic nose (E-nose) system (Alpha M.O.S. SA, Toulouse, France), HS100 Headspace auto sampler (Alpha M.O.S. SA, Toulouse, France), Fox 3000 software (Alpha M.O.S. SA, Toulouse, France)

An Alpha MOS Fox 3000 E-nose system with two metal oxide sensor arrays (consisting of 12 sensors) was used for qualitative and quantitative analysis of residual solvents. Figure 3.1 shows the Alpha MOS Fox 3000 e-nose system. It consists of three main components: an agitator, a headspace auto sampler, and sensor arrays. The agitator is the place where the vials are heated up in order to generate the headspace vapor from the samples. The auto sampler collects the headspace vapor and injects it into the sensor array. The sensor array consists of 12 metal oxide sensors. Each sensor has different sensitivity and selectivity to various chemical compounds. Therefore, a combination of several sensors provides a unique fingerprint of the samples. This allows to track any variation in the headspace of the samples. Figure 3.2 shows an example of sensor responses as a function of time for one of the model solvents. In this figure the sensor responses are represented by the relative resistance change, $(R_0 - R) / R_0$, where R_0 is the minimum of the resistance reading during the baseline purge and R is the maximum resistance reading during the vapor exposure. The data extracted from sensor responses can be used to detect, characterize, identify, and eventually quantify the volatiles.

The optimized e-nose set up parameters are shown in Table 3.3. The detailed optimization procedure is explained in section 3.2.3.

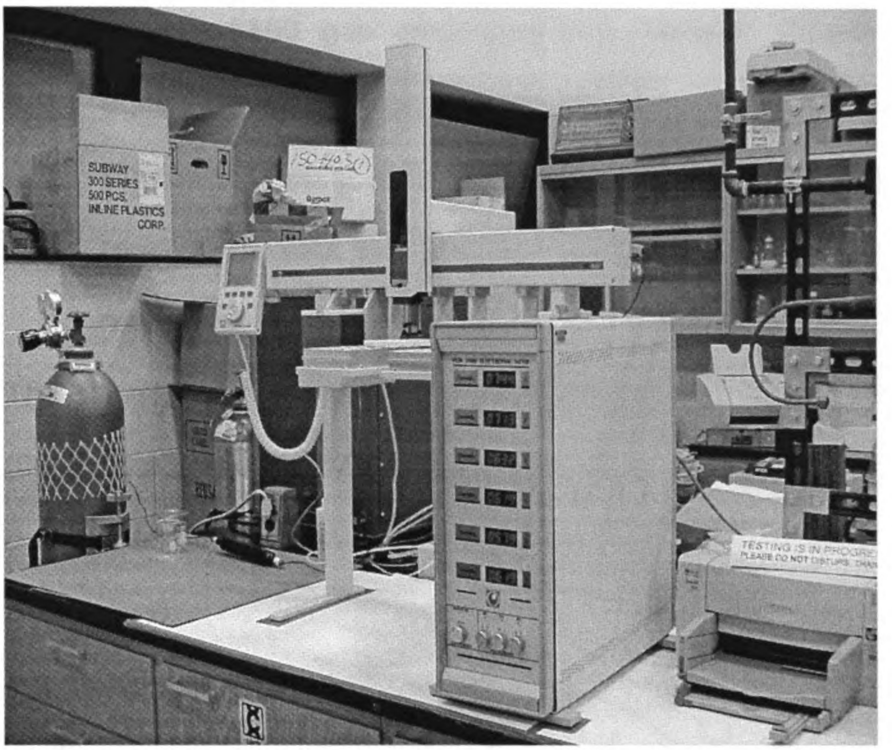

Figure 3.1: Alpha MOS Fox 3000 e-nose system

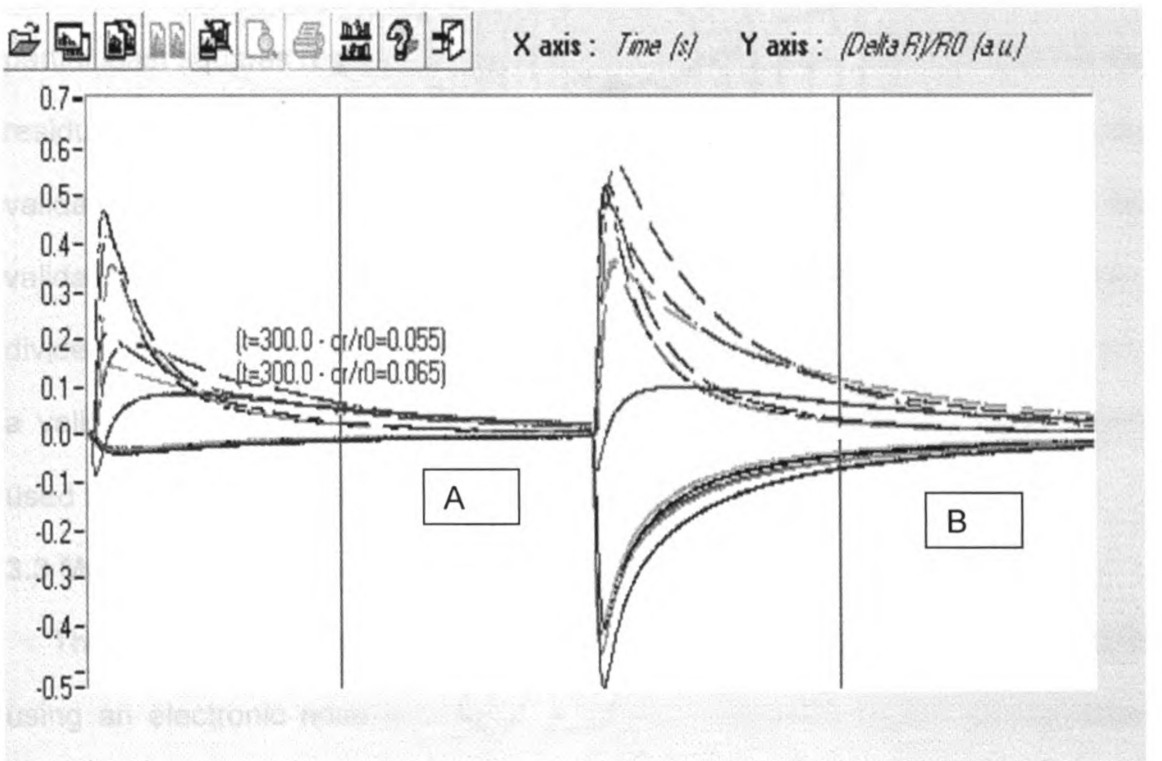

Figure 3.2: Typical e-nose sensor response curves for ethyl acetate samples
[A: ethyl acetate samples (1µl), B: ethyl acetate samples (10µl)]

- An HP 6890 gas chromatograph (Hewlett- Packard, Avondale, PA), equipped with a gas flame ionization detector and interfaced with Empower-Waters software was used for quantitative analysis of the residual solvents in LDPE films. All the data were recorded as peak area response.

The column used in this study was Supelcowax 10 fused silica capillary column (60 m, 0.25 mm ID, 0.25 μm film thickness) (Supelco Inc., Bellefonte, PA). A detailed summary of the GC conditions employed in this study is presented in Appendix B.

3.2 Statistical Analysis

The responses obtained from the sensor arrays were processed using principle component analysis (PCA), discriminate factorial analysis (DFA), and partial least squares regression analysis (PLS) in order to qualify and quantify the residual solvents. The models obtained from DFA and PLS analysis were validated by means of the partial cross-validation (leave-one-out) method. In this validation method, the data sets obtained during measurements were randomly divided into a training set, used for building up the model (learning process), and a validation set, used for validation purposes. Finally, unknown samples were used to check the performance of the new model.

3.3 Method Development

The method development for assessing the residual solvents from LDPE using an electronic nose consists of four main steps which are representative

VOC selection, sample preparation, e-nose parameter optimization, and building a model. Figure 3.3 illustrates the main steps of the method development.

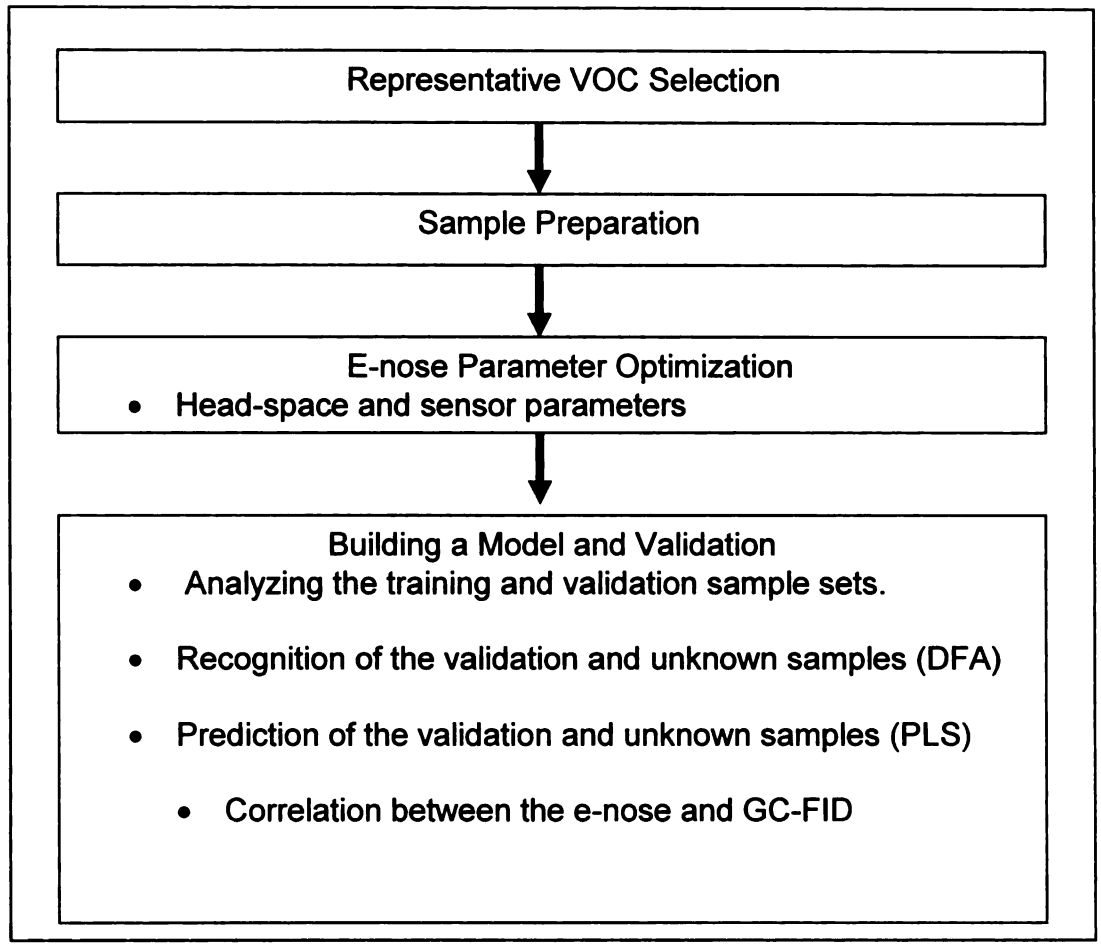

Figure 3.3: The steps of method development

3.3.1 Representative VOC Selection

In this study, ethyl acetate, ethyl alcohol, and toluene were chosen to represent different solvent categories used in printing ink and adhesive formulations.

3.3.2 Sample Preparation

LDPE film samples were prepared by the method described by Suman et al. (2003). The samples were cut into 2 x 25 cm strips and then placed into glass jars. Filter paper inserted into each jar lid was injected with 1.0, 2.5, 5.0, 7.5, or 10 µl of the solvent. Then, the jars were tightly closed. The sealed jars were kept at 50°C for three hours, and then at room temperature for one day in order to equilibrate the solvent in the headspace of the jar. After this treatment, the films were used to prepare headspace vials for the e-nose and GC analysis. A diagram summarizing the sample preparation and experimental steps is shown in Figure 3.4.

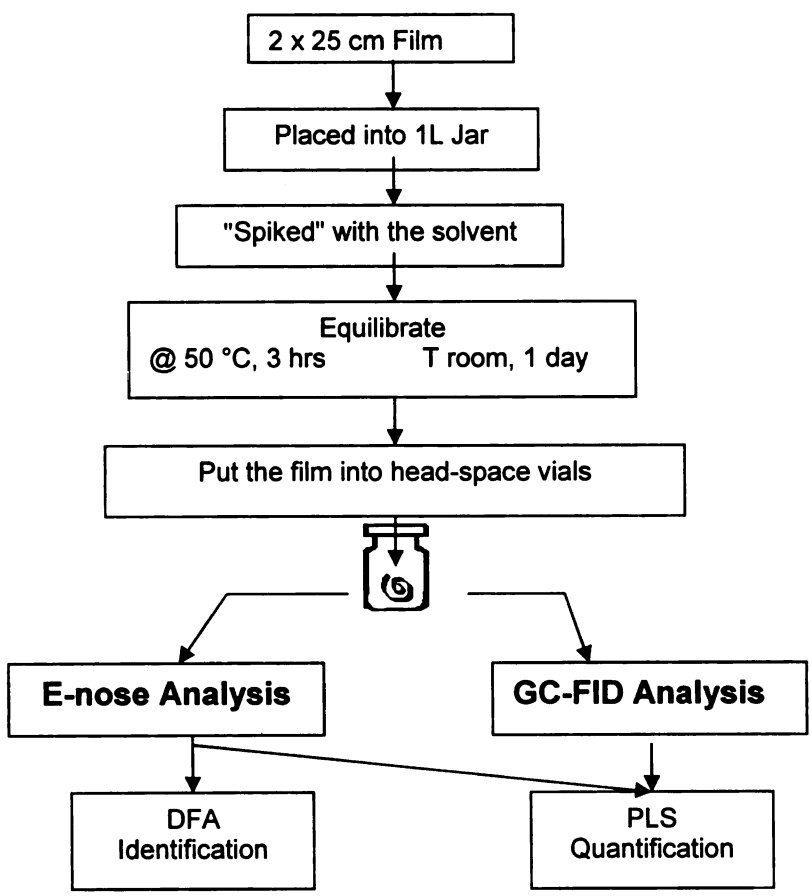

Figure 3.4: Sample preparation and experimental steps.

3.3.3 E-nose Parameter Optimization

The aim of method development is to select operating conditions for an e-nose analysis which are consistent and reliable. There are several important parameters that need to be optimized to obtain the maximum performance from the e-nose (Alpha MOS Fox 3000 Manual, 2001). Therefore, before taking the real measurements, a number of preliminary tests were made in order to find optimum analysis conditions which were acceptable for all of the solvent samples.

There were thirteen variables that could be controlled directly in the system: incubation time, incubation temperature, syringe temperature, syringe type, filling speed, flushing time, injection volume, injection speed, vial size, acquisition time, acquisition period, agitation speed, and delay. To minimize unnecessary complexity, all efforts were directed towards only the two most important parameters, incubation temperature and vial size (Deventer and Mallikarjunan, 2002; Alpha MOS Fox 3000 Manual, 2001). The rest of the parameters were set up as shown in Table 3.3.

Incubation Temperature:

The incubation temperature can be considered one of the salient parameters that must be controlled since the generation of head-space volatiles varies with the temperature. Any variation in the temperature may result in changes in volatile concentrations in the head-space (Van Deventer and Mallikarjunan, 2002). Consequently, the changes in volatile concentrations would directly affect

the sensor responses. Table 3.1 shows how the temperature affects the e-nose analysis results.

Table 3.1: Effect of incubation temperature on discrimination indexes for ethyl acetate, ethyl alcohol, and toluene.

Trial	Incubation Temperature, °C	Discrimination Index PCA
1	50	82
2	**60**	**93**
3	75	87

The Alpha MOS Fox 3000 Manual (2001) recommended that the incubation temperature should be set between 40 and 50°C for highly volatile compounds and between 80 and 100°C for less volatile compounds.

Van Deventer and Mallikarjunan (2002) compared the performance of three commercial e-nose systems in terms of detection of volatiles from printed plastic packaging films. In this study, the volatile compounds of interest were not specifically named due to a confidentiality disclosure agreement with the manufacturer; however, the setting parameters for the Fox 3000 e-nose were reported. The optimum incubation temperature that was chosen for this study was 75°C.

Suman et al. (2003) also analyzed six different solvents in order to identify and control the retained solvents in printed films. In this study, an incubation temperature of 60°C was used.

Consequently, on the basis of previous studies, the incubation temperature was studied within the range of 50 – 75°C. Figures 3.5, 3.6, and 3.7 illustrate the

plots of PCA for LDPE film samples with three solvents at three different temperatures. As can be seen, the film samples were easily discriminated at 50, 60 and 75°C using principle component analysis (PCA). Since there was no intersection among three sample groups, high discrimination indices were obtained (82 for 50°C, 93 for 60°C, and 87 for 75°C). Generally, the higher the discrimination index, the better is the discrimination between the groups (Alpha MOS Fox 3000 Manual, 2001). In this study, increasing the incubation temperature from 50°C to 60°C did give us a higher discrimination index, whereas increasing the incubation temperature from 60°C to 75°C did not provide us any significant differences in discrimination index and sensor responses. Therefore, the incubation temperature was optimized at 60°C.

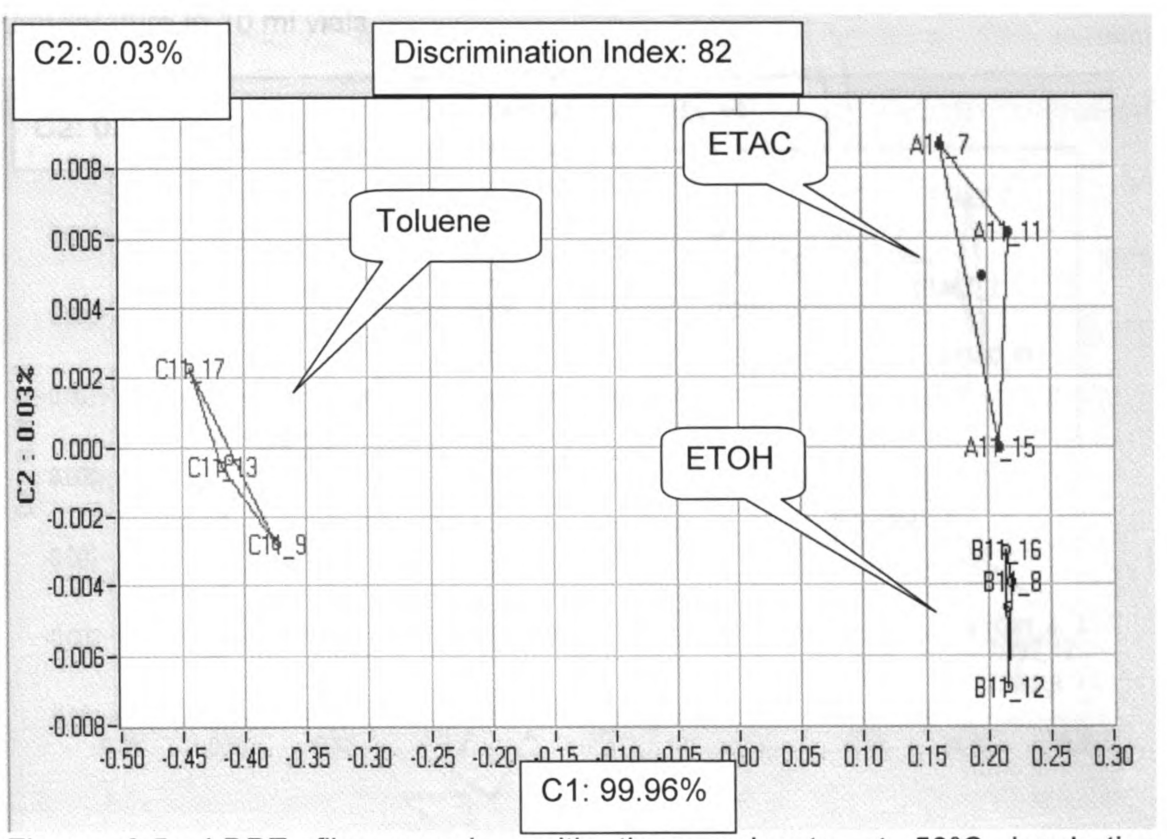

Figure 3.5: LDPE film samples with three solvents at 50°C incubation temperature in 10 ml vials.

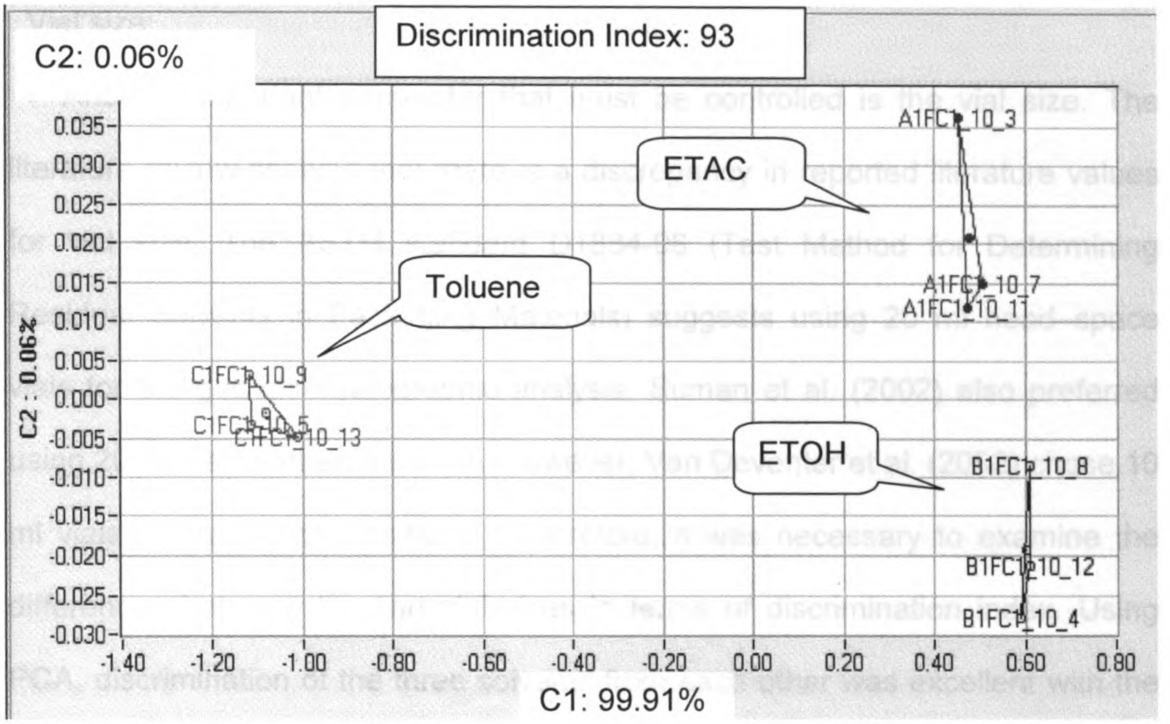

Figure 3.6: LDPE film samples with three solvents at 60°C incubation temperature in 10 ml vials.

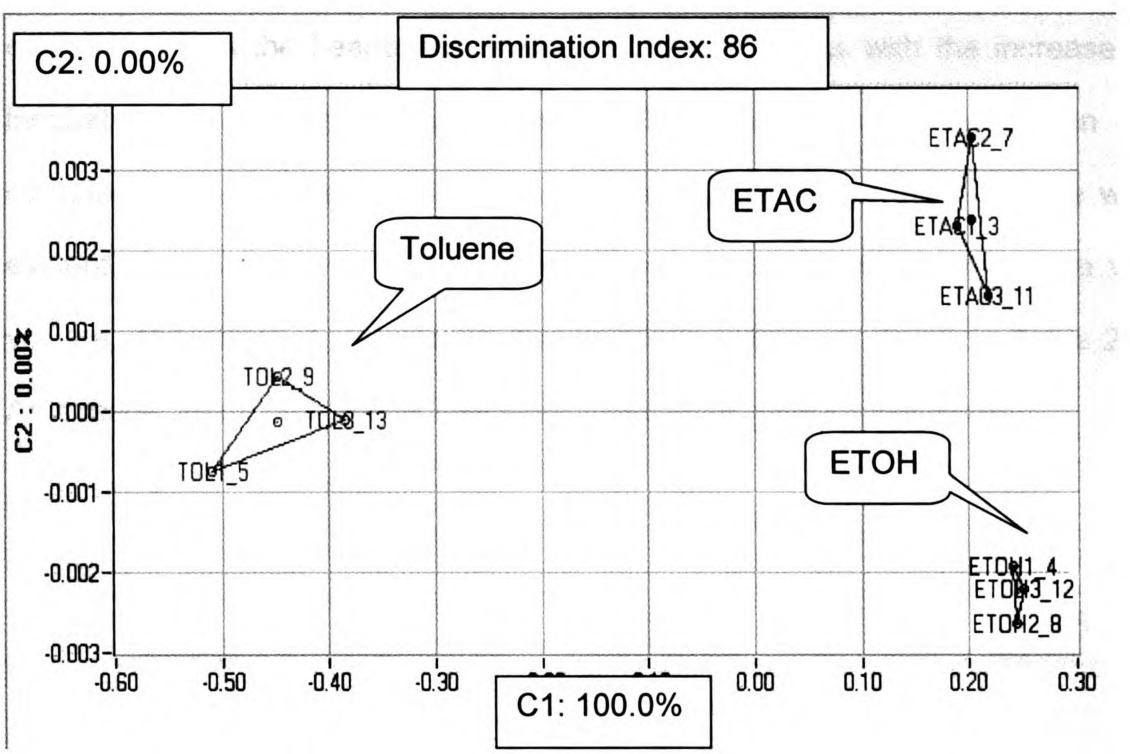

Figure 3.7: LDPE film samples with three solvents at 75°C incubation temperature in 10 ml vials.

Vial size:

Another important parameter that must be controlled is the vial size. The literature review showed that there is a discrepancy in reported literature values for vial size. The ASTM standard D1884-98 (Test Method for Determining Residual Solvents in Packaging Materials) suggests using 20 ml head–space vials for the gas chromatographic analysis. Suman et al. (2002) also preferred using 20 ml vials in their research. However, Van Deventer et al. (2002) chose 10 ml vials for the e-nose analysis. Therefore, it was necessary to examine the differences between the two vial sizes in terms of discrimination index. Using PCA, discrimination of the three solvents from each other was excellent with the 10 ml vials, while discrimination failed with the 20 ml vials. It is well known that the sensor responses depend on the incubation temperature. The solvent concentration in the headspace of the vial also increases with the increase of incubation temperature. Consequently, a high discrimination index can be obtained. But, in the case of 20 ml vials, incubation temperature or time was evidently not enough to get maximum sensor responses due to the large vial volume. The effect of vial size on discrimination indices is shown in Table 2.2. As a result, 10 ml headspace vials were found to be ideal for this study.

Table 3.2: Effect of vial size on discrimination indices.

Trial	Incubation Temperature, °C	Vial Size, ml	Discrimination Index PCA
1	60	10	93
2	60	20	0

On the basis of these preliminary tests, the incubation temperature of 60°C and 10 ml vial size were found to be perfect for this study. These conditions gave the highest discrimination index, which was also evidence of higher sensor responses. After optimization of e-nose parameters, in order to control the repeatability of the sample preparation and e-nose data acquisition parameters, the LDPE films were spiked with the solvents by the method described in section 3.3.2 and then analyzed by using PCA. We obtained exactly the same discrimination index value as in previous measurements, which is evidence of the repeatability of the method (Figure 3.8).

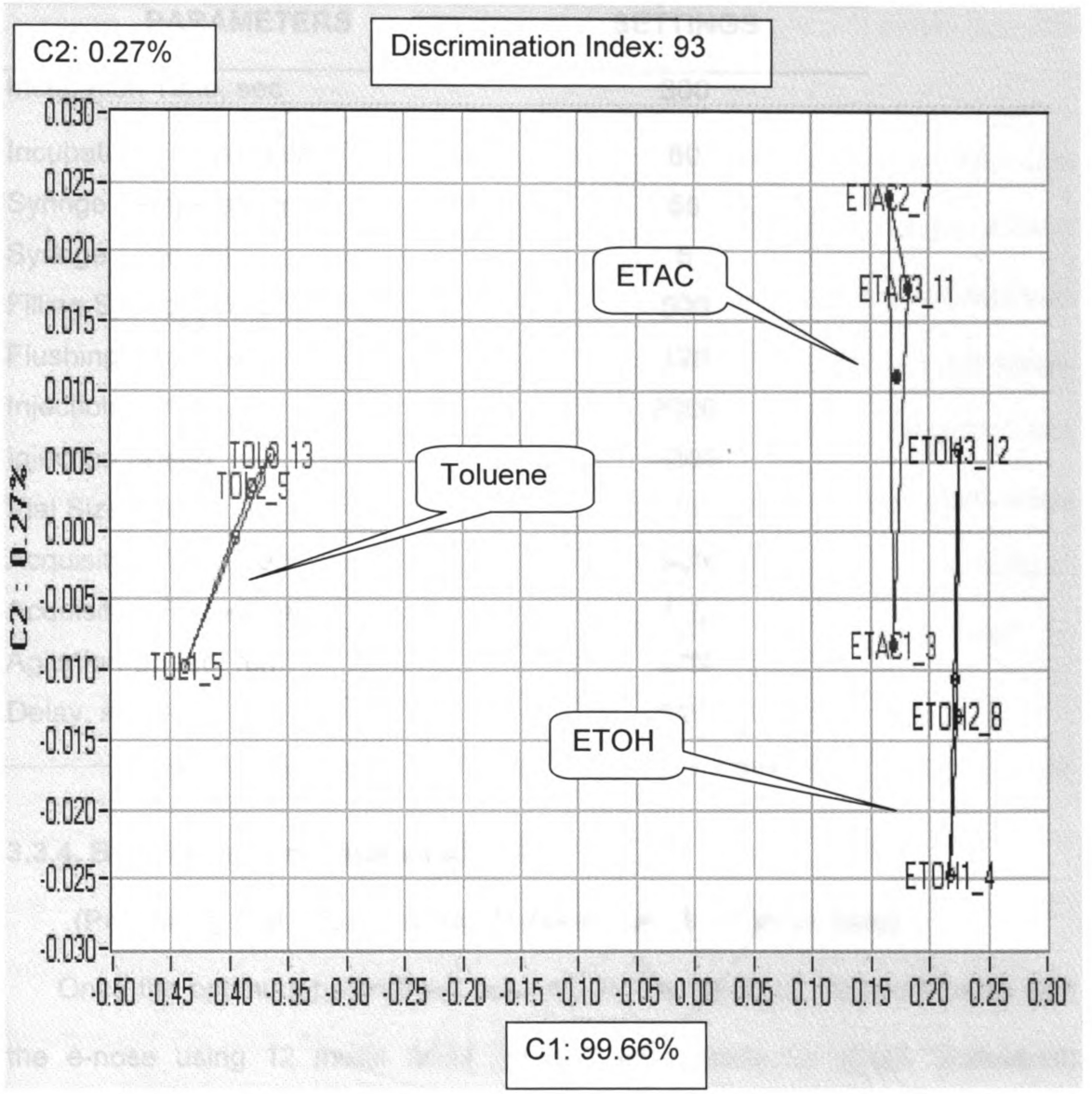

Figure 3.8: LDPE film samples with three solvents at 60°C incubation temperature in 10ml vials (Repeated procedure)

Table 3.3 : Optimized data acquisition parameters.

PARAMETERS	SETTINGS
Incubation Time, sec	300
Incubation Temperature, °C	60
Syringe Temperature, °C	65
Syringe Type, ml	5
Filling Speed, µl/sec	500
Flushing Time, sec	120
Injection Volume, µl	2000
Injection Speed, µl	2000
Vial Size, ml	10
Acquisition Time, sec	600
Acquisition Period, sec	0.5
Agitation Speed, rpm	500
Delay, sec	900

3.3.4. Building a Model and Validation

(Preparing and Analyzing the Training and Validation Sets)

Once the optimum parameters were set for the samples, measurements with the e-nose using 12 metal oxide sensors were made for single (individual) solvents, and binary mixtures of the three solvents. The single solvent groups were composed of three solvents; ethyl acetate, ethyl alcohol, and toluene. The data sets for the single solvents were prepared by using different injection amounts (1.0, 2.5, 5.0, 7.5, and 10 µl). Five replicates were used for each single solvent and their varying injection amounts. The data sets for the binary mixtures were prepared for the three different solvent combinations using varying injection

amounts (1.0, 2.5, and 7.5 µl). Three replicates were used for the binary mixtures. Table 3.4 shows the injection amounts of the single and binary solvents at different concentrations.

The data matrix for one injection amount was constructed with 180 data points, which were the responses from 12 sensors for three single solvent samples with the five replicates (12 X 3 X 5 = 180). As can be seen, the data sets for the e-nose are multivariate and difficult to interpret. Therefore, it is necessary to employ multivariate statistics in order to assess the classification and quantification of the solvents in the LDPE films. The most common multivariate statistical techniques, principle component analysis (PCA), discriminate factorial analysis (DFA), and partial least squares analysis (PLS), were used for qualification and quantification of the samples.

PCA is an unsupervised learning technique which allows reduction of multi-dimensional data to two dimensions while simplifying the interpretation of the data (Delpha et al., 2001). For instance, the responses from 12 sensors (12 dimensions) can be processed and displayed in two dimensions. This allows us to interpret the data easily. In addition, the samples can be classified without prior information on the nature of the samples. Conversely, DFA and PLS require prior knowledge about the samples. DFA is a supervised learning technique which classifies the samples by developing a model and then identifies the unknown samples in qualitative analysis. PLS is an algorithm based on linear regression techniques. It is also used to build a model that is able to predict the quantitative information for the samples (Alpha MOS Fox 3000 Manual, 2001).

Table 3.4: The combination of ethyl acetate, ethyl alcohol, and toluene at varying injection amounts.

	Percent Concentration (v/v)			Amounts of Injection (µl)				
	ETAC (A)	ETOH (B)	TOL (C)	1.0	2.5	5.0	7.5	10
5 Replicates	100	0	0	✓	✓	✓	✓	✓
	0	100	0	✓	✓	✓	✓	✓
	0	0	100	✓	✓	✓	✓	✓
3 Replicates	30	70	0	✓	✓		✓	
	50	50	0	✓	✓		✓	
	70	30	0	✓	✓		✓	
	30	0	70	✓	✓		✓	
	50	0	50	✓	✓		✓	
	70	0	30	✓	✓		✓	
	0	30	70	✓	✓		✓	
	0	50	50	✓	✓		✓	
	0	70	30	✓	✓		✓	

In general, these algorithms can only be considered as valid when the data (sensor response pattern) is well distributed in their domain. However, in many cases the patterns from different classes can overlap. The overlapping groups could lead us to believe that there is no difference between the samples (Goodner, 2001). Thus, it is necessary to detect and remove outliers from the data sets. The data sets were studied using PCA ,which is the best way to detect rapidly the outliers (Alpha MOS Fox 3000 Manual, 2001). Among all the

measurements, only one sample was found to be an outlier and discarded from the data set. A new sample was added to the data set. The outlier detection method based on comparing the cluster shapes in PCA and analyzing the sensor profiles is described in Appendix C.

After eliminating the outliers, the next step was a training phase. During this phase, the algorithm is trained by the samples whose classifications are known, and then this algorithm can be used to classify the unknown samples. It is clear that the algorithm can only classify the unknown samples if they exhibit the same behavior as the training samples (Carmel et al., 2003). As in all quantitative methods, it is important to use training samples containing all expected ranges of the future unknown samples (Vlasov and Legin, 1998). Therefore, in this study, varying injection amounts for the single and binary solvents were used. The data (the sensory response patterns) were divided into a training set and a validation set. For the samples with five replicates, three replicates were randomly selected for training the algorithm, and the remaining two replicates were used for the validation. For the samples with three replicates, two replicates were selected for the training set, and one replicate for the validation set. The validation data sets were used to validate the algorithm.

When the identification and validation were achieved on the DFA model, estimation of the sample quantity was done by PLS analysis. The PLS analysis was applied to the samples in order to assess the relationship between predicted and experimental values for the concentration of the single and binary solvents. For building the calibration curves for the single and binary solvent mixtures, pre–

determined GC area responses were used as a concentration value. Validation of the PLS model was done by evaluating the correlation coefficient and using a modified leave-one out method where one randomly chosen sample was removed from the dataset and considered as an "unknown" sample.

In the traditional, leave-one out method (cross validation method), each data point in turn is removed from the data set and tested as unknown using the remaining data points. In this research, in order to minimize the unnecessary complexity, a modified leave-one out method which omitting only one data point was used.

Finally, in order to test the performance of the model, unknown test samples were projected on the PLS model.

4. RESULTS AND DISCUSSION

4.1 Identification of the Single Solvents

Figure 4.1, 4.2, and 4.3 illustrate the DFA plots of ethyl acetate, ethyl alcohol, and toluene with different injection amounts, respectively. In these figures, the data clusters which belong to different injection amounts were separated from each other. It is interesting to note that the separation for all model solvents followed similar patterns.

Figure 4.4 shows the DFA plots combining ethyl acetate, ethyl alcohol, and toluene training sets at different injection amounts. The model developed by the training sets was applied to the validation data set ("unknown samples"). Figure 4.5 shows the identification of single solvent validation sets. As can be seen, the validation data sets (so called "unknown" samples) were mostly placed into the correct solvent category. The validation data set scores are listed in Table 4.1. The first column gives the codes of the validation data sets. The second column indicates whether or not the validation data sets were recognized. The third column also indicates the solvent categories (groups) and the last column shows the percentage of recognition of the samples. Using this percentage, we can understand how far the validation samples are from their recognized groups. If the validation samples are in the group, the percentage is 100%. The overall percentage correct identification rates for the validation data sets are also presented in Table 4.2. All ethyl alcohol and toluene samples were identified correctly (100% correct recognition). Out of 10 ethyl acetate samples, only one sample - ethyl acetate (1μl) - was misidentified as ethyl alcohol. However, the

overall percentage of correct identification for ethyl acetate was found to be 90% (Table 4.2). Hence, we can conclude that the e-nose is capable of clear recognition of "unknown" single solvent samples.

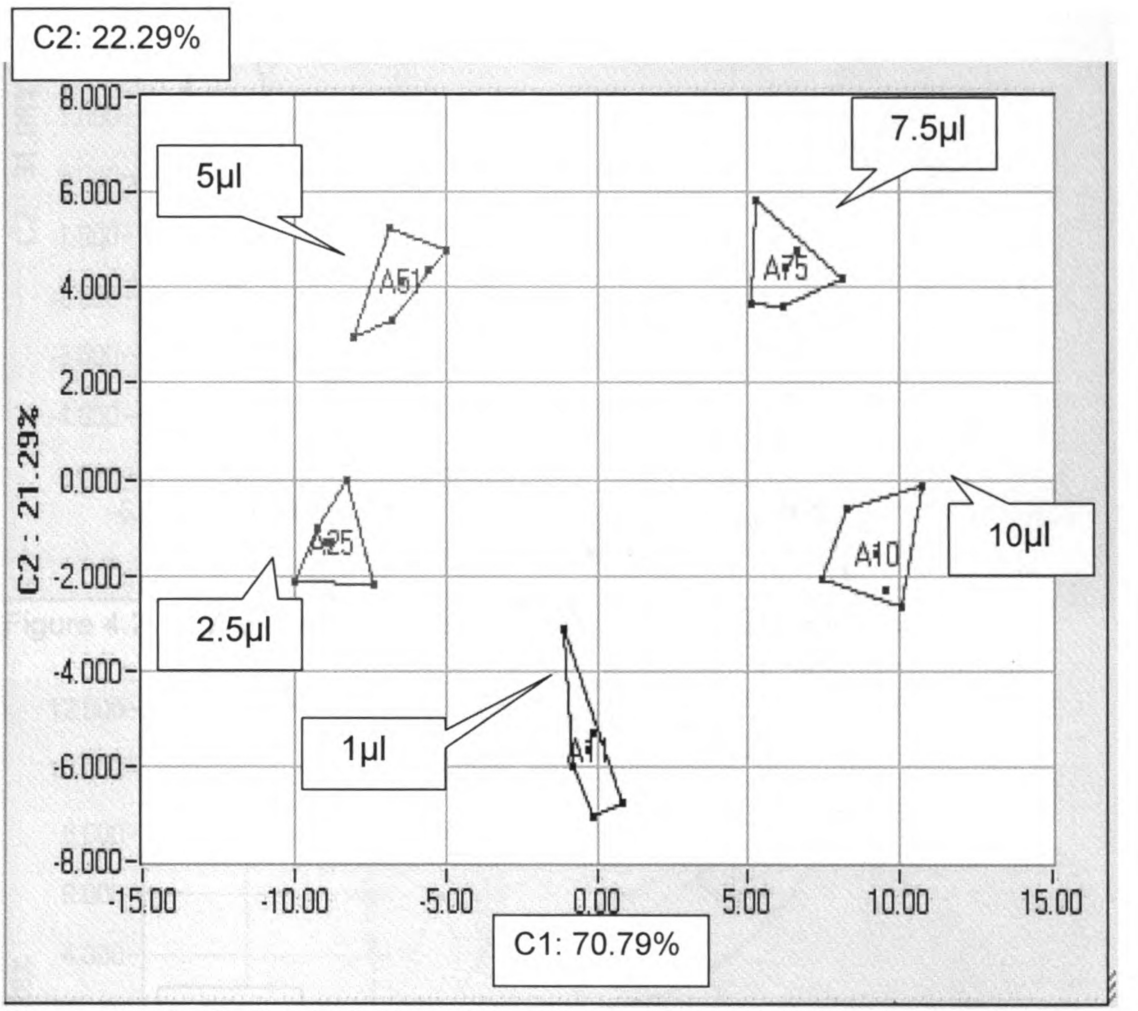

Figure 4.1: DFA plot of ethyl acetate with five different injection amounts

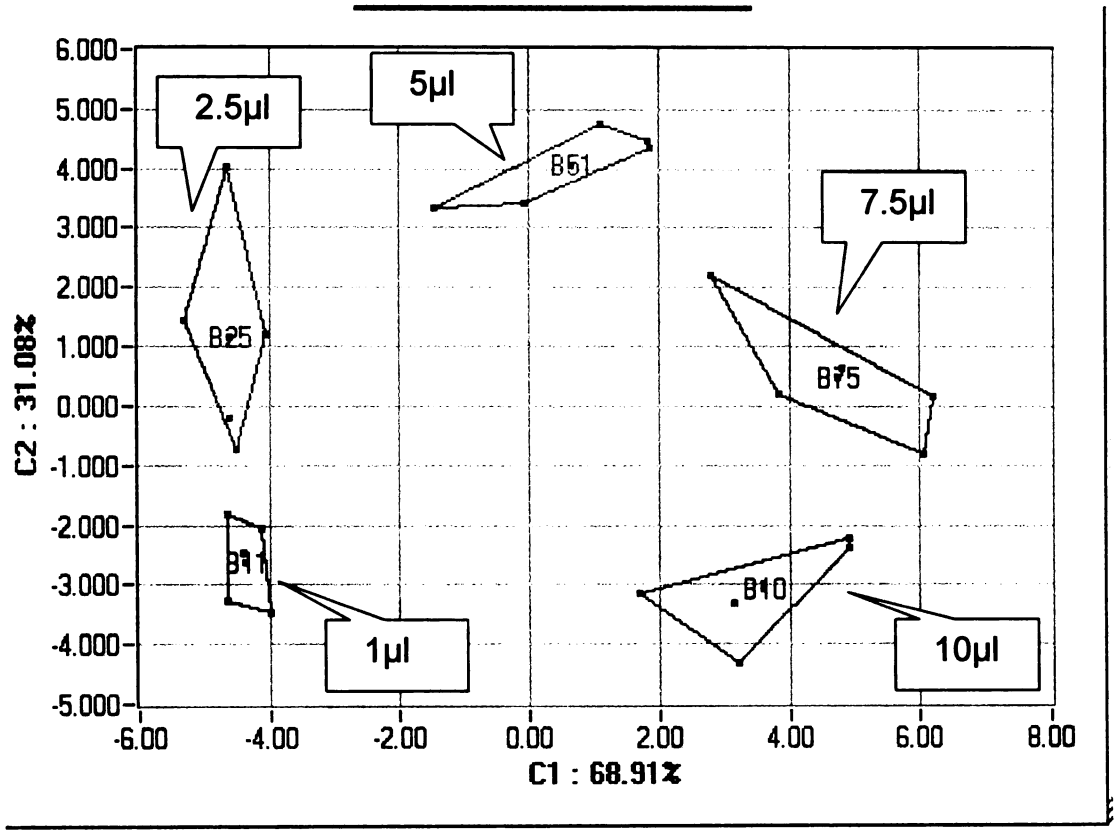

Figure 4.2: DFA plot of ethyl alcohol with five different injection amounts

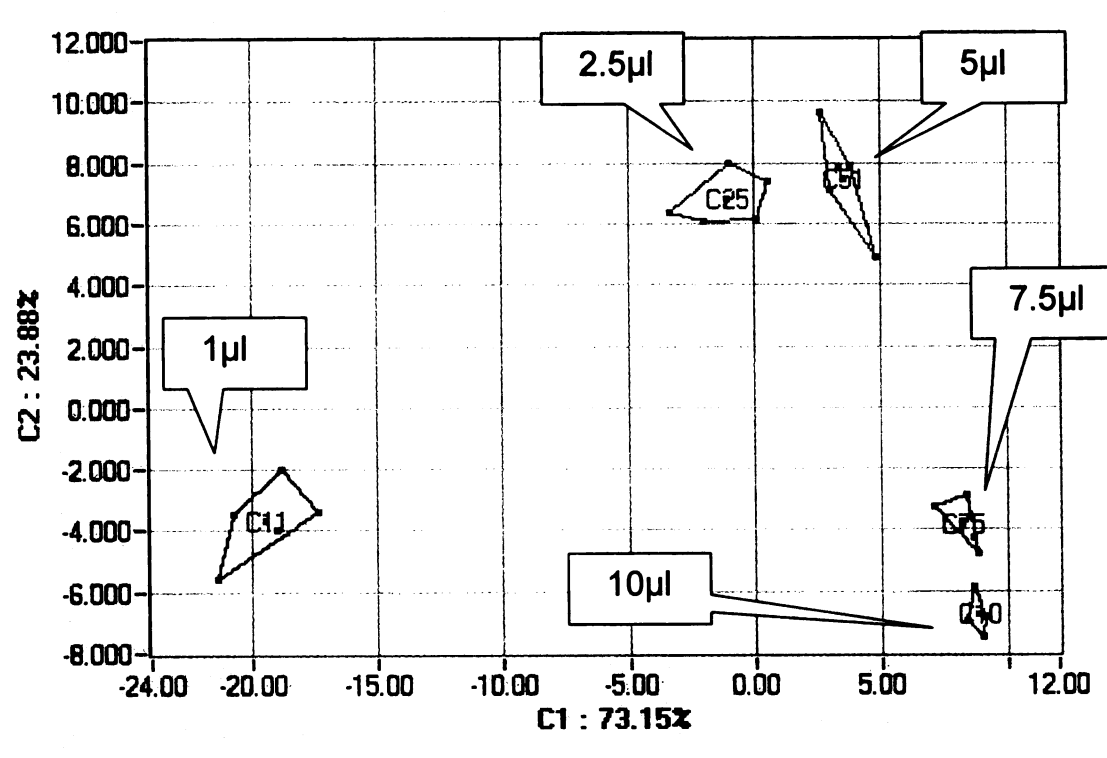

Figure 4.3: DFA plot of toluene with five different injection amounts

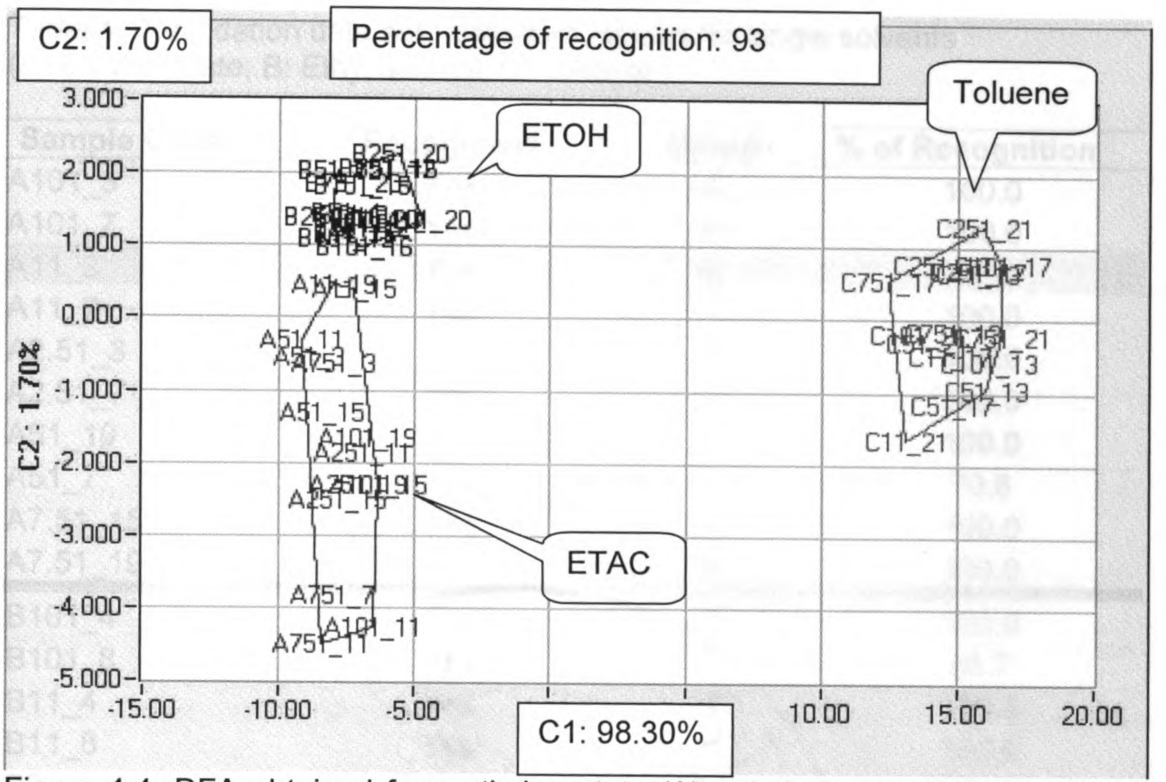

Figure 4.4: DFA obtained from ethyl acetate (A), ethyl alcohol (B), and toluene (C) training samples.

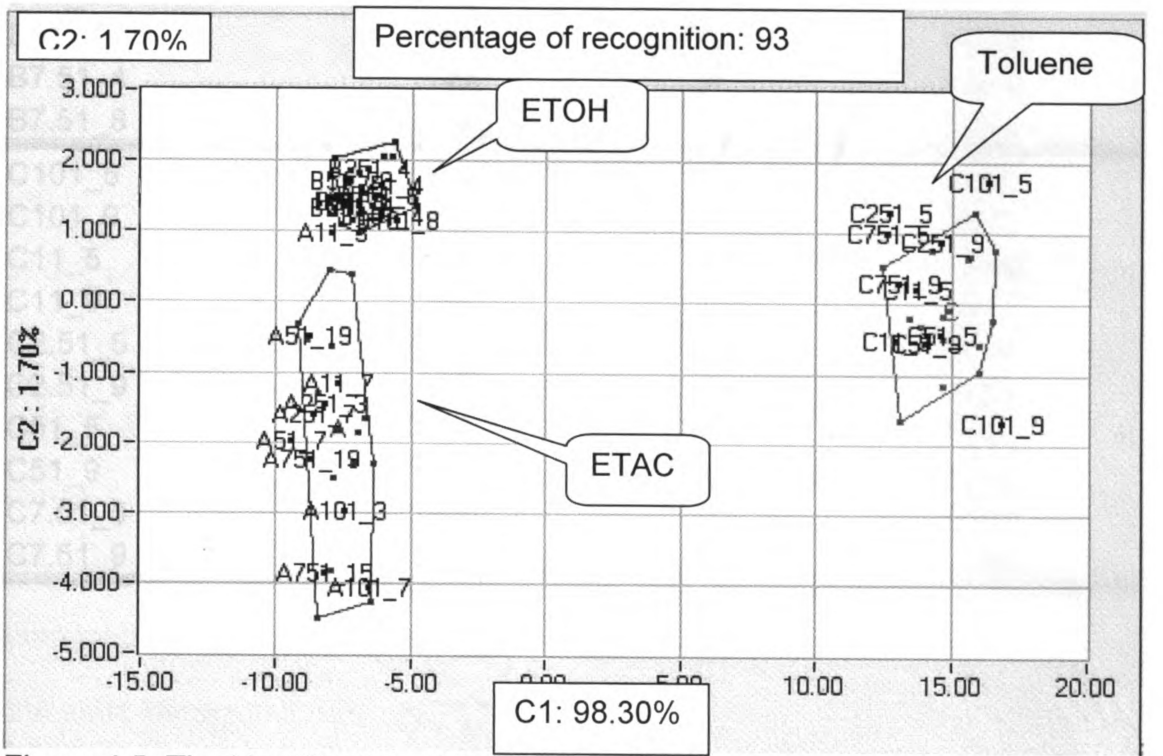

Figure 4.5: The identification of the single solvent validation data set using DFA.

Table 4.1: Validation data set "unknown" scores for single solvents
(A: Ethyl acetate, B: Ethyl alcohol, C: Toluene)

Sample Code	Recognized	Group	% of Recognition
A101_3	Yes	A	100.0
A101_7	Yes	A	100.0
A11_3	Yes	B	82.8
A11_7	Yes	A	100.0
A2.51_3	Yes	A	100.0
A2.51_7	Yes	A	100.0
A51_19	Yes	A	100.0
A51_7	Yes	A	70.8
A7.51_15	Yes	A	100.0
A7.51_19	Yes	A	100.0
B101_4	Yes	B	100.0
B101_8	Yes	B	83.7
B11_4	Yes	B	100.0
B11_8	Yes	B	100.0
B2.51_4	Yes	B	100.0
B2.51_8	Yes	B	100.0
B51_20	Yes	B	100.0
B51_8	Yes	B	100.0
B7.51_4	Yes	B	100.0
B7.51_8	Yes	B	100.0
C101_5	Yes	C	99.5
C101_9	Yes	C	98.7
C11_5	Yes	C	100.0
C11_9	Yes	C	100.0
C2.51_5	Yes	C	97.9
C2.51_9	Yes	C	100.0
C51_5	Yes	C	100.0
C51_9	Yes	C	100.0
C7.51_5	Yes	C	99.2
C7.51_9	Yes	C	100.0

Table 4.2: Identification results of the DFA for single solvents validation data set. (A: Ethyl acetate, B: Ethyl alcohol, C: Toluene)

Code	A	B	C	% Correct Identification
A	9	1	0	**90**
B	0	10	0	**100**
C	0	0	10	**100**

4.2 Identification of the Binary Solvents

Figure 4.6, 4.7, and 4.8 illustrate the DFA plots of toluene:ethyl alcohol, ethyl acetate:ethyl alcohol, and ethyl acetate:toluene mixtures with different combinations (30:70, 50:50, 70:30, 100:0 (v/v)), respectively. In these figures, the data sets for different solvent combinations were clearly separated from each other.

Figure 4.9 shows the DFA plots of binary solvent training sets at different injection amounts. The model developed by the training sets was applied to validation data sets ("unknown samples"). Figure 4.10 shows the identification of binary solvent validation sets. The validation data set scores are listed in Table 4.3. The first column gives the codes of the validation data sets. The second column indicates whether or not the validation data sets were recognized. The third column indicates the solvent categories (groups) and the last column shows the percentage of recognition of the samples. Using this percentage, we can understand how far the validation samples are from their recognized groups. If the samples are in the group, the percentage is 100%. The overall percentage correct identification rates for the validation data sets are presented in Table 4.4.

ETAC/ETOH with all its combinations was identified correctly (100% correct recognition). However, ETAC/TOL, TOL/ETOH and their combinations were misidentified. Out of 9 ETAC/TOL samples, one sample was misidentified as TOL/ETOH. Out of 9 TOL/ETOH samples, three samples were misidentified as ETAC/TOL. The overall percentage of correct identification for ETAC/TOL and TOL/ETOH were found to be 88% and 66%, respectively. As can be seen, the e-nose was able to recognize ETAC/ETOH solvent mixtures whereas it can only partially recognize ETAC/TOL and TOL/ETOH samples. It is important to note that when we considered the DFA analysis just within the same solvent mixture groups, a perfect separation was observed (Figures 4.6 – 4.8). But, when we performed the DFA analysis for all binary solvent mixtures, some of the data slightly overlapped (Figures 4.9 and 4.10). Consequently, this led to the misclassification on the DFA plots. Another reason for the misclassification might be the differences in solvents' polarity. Ethyl acetate and ethyl alcohol are polar solvents whereas toluene is a non-polar solvent. Therefore, non-polar LDPE film samples might be attracted to the non-polar toluene and tend to retain toluene molecules relatively more than ethyl acetate and ethyl alcohol molecules. This problem may be overcome by changing the e-nose setup parameters.

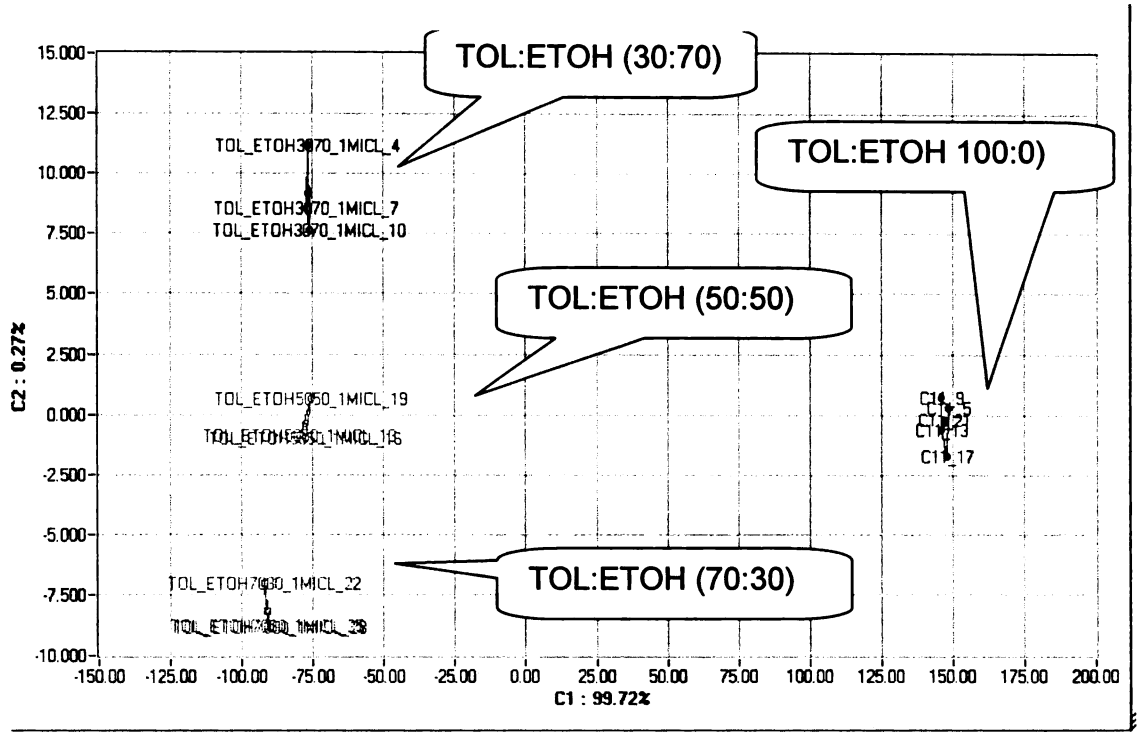

Figure 4.6: DFA plot of toluene and ethyl alcohol mixtures with different combinations (30:70 , 50:50, 70:30, 100:0 v/v) - injection amount 1µl.

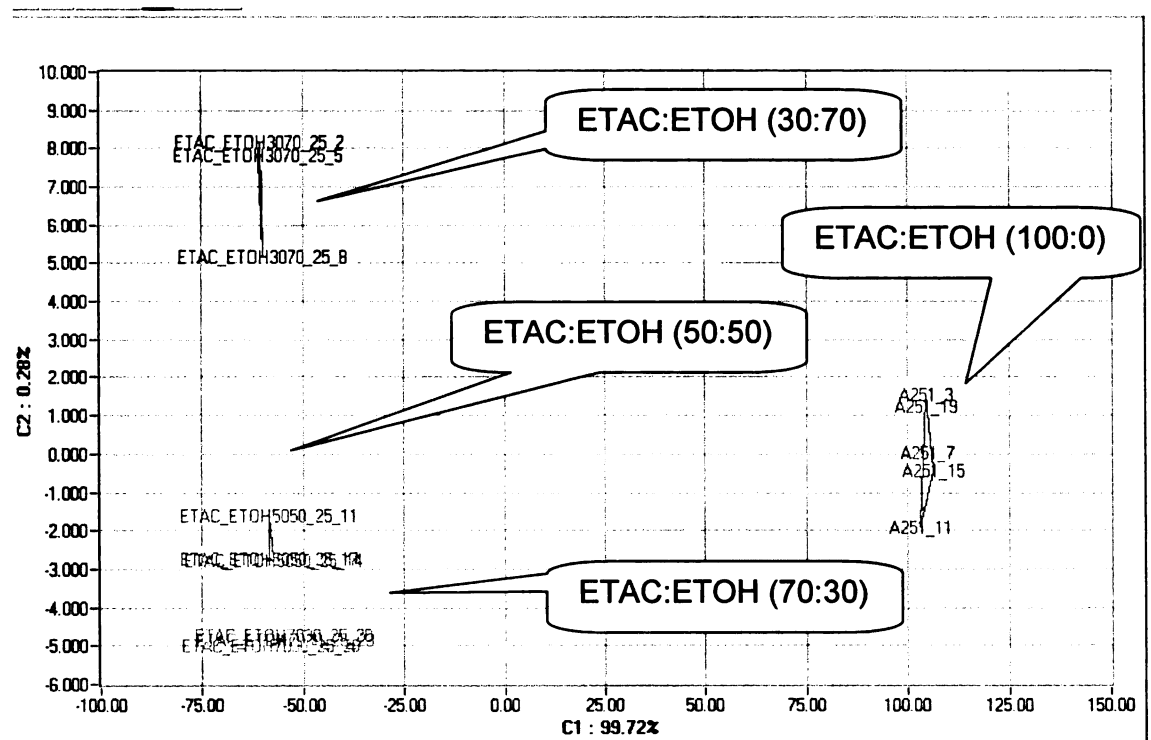

Figure 4.7: DFA plot of ethyl acetate and ethyl alcohol mixtures with different combinations (30:70 , 50:50, 70:30, 100:0 v/v) - injection amount 1µl.

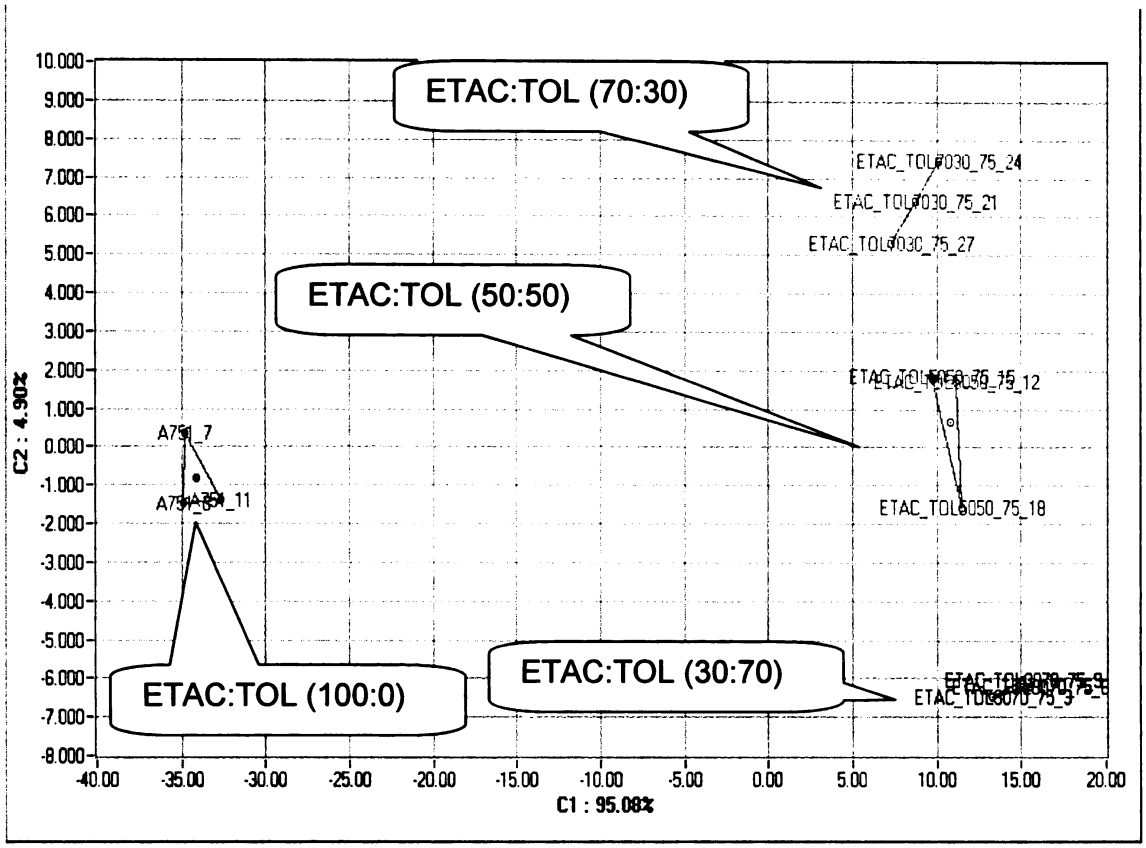

Figure 4.8: DFA plot of ethyl acetate and toluene mixtures with different combinations (30:70 , 50:50, 70:30, 100:0 v/v) - injection amount 1µl.

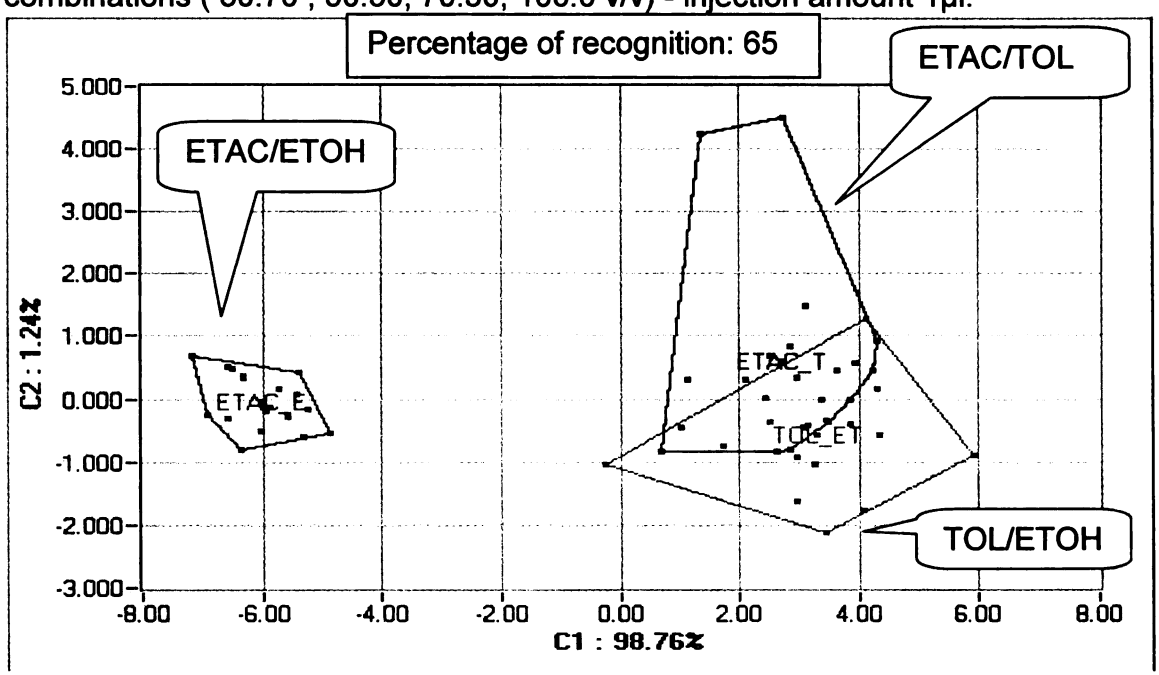

Figure 4.9: DFA obtained from binary solvent training sets; ETAC/ETOH (30:70, 50:50, 70:30), ETAC/TOL (30:70, 50:50, 70:30), TOL/ETOH (30:70, 50:50, 70:30).

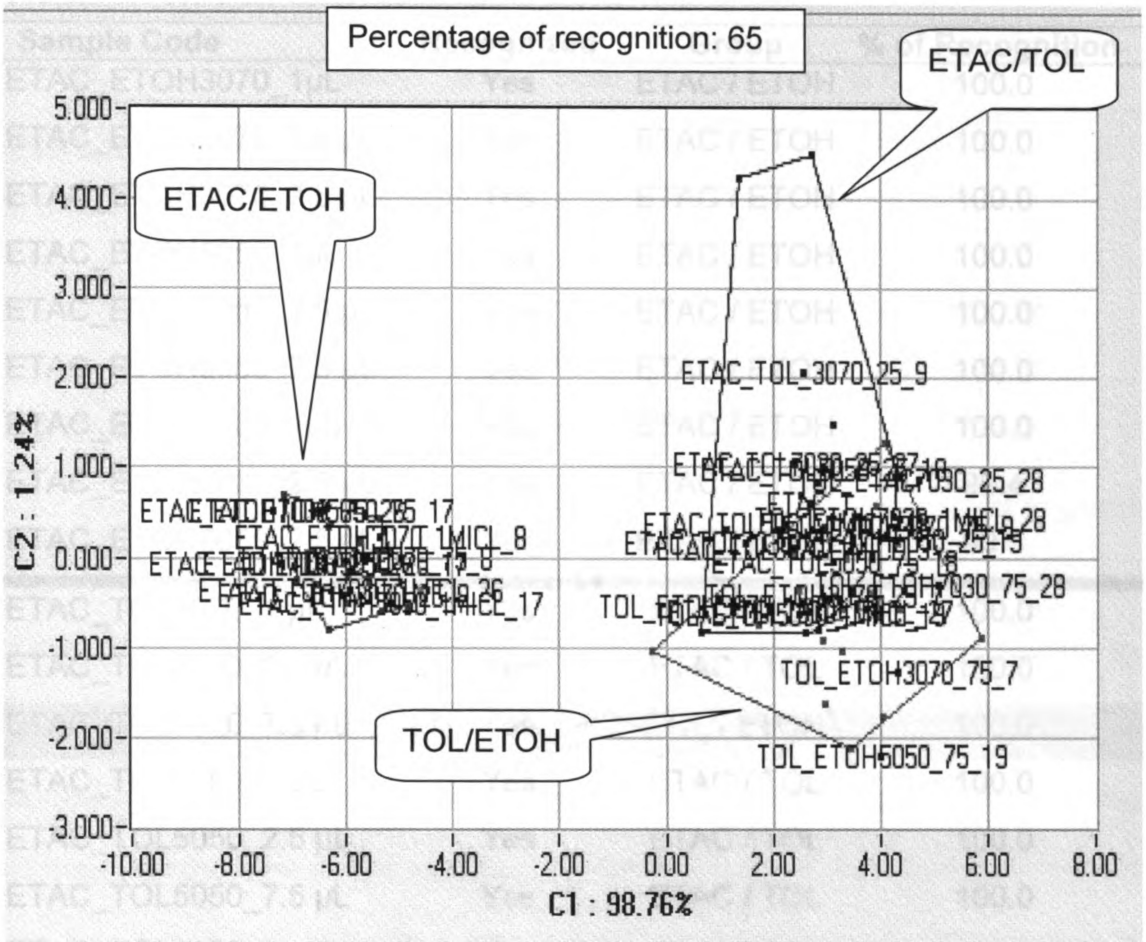

Figure 4.10: The identification of the binary solvents - validation data sets (" unknown" samples) using DFA

Table 4.3: Validation data set "unknown" scores for binary solvents.

Sample Code	Recognized	Group	% of Recognition
ETAC_ETOH3070_1μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH3070_2.5 μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH3070_7.5 μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH5050_1μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH5050_2.5 μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH5050_7.5 μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH7030_1μL	Yes	ETAC / ETOH	100.0
ETAC_ETOH7030_2.5 μL	Yes	ETAC / ETOH	99.4
ETAC_ETOH7030_7.5 μL	Yes	ETAC / ETOH	99.3
ETAC_TOL3070_1 μL	Yes	ETAC / TOL	100.0
ETAC_TOL3070_2.5 μL	Yes	ETAC / TOL	100.0
ETAC_TOL3070_7.5 μL	Yes	TOL / ETOH	100.0
ETAC_TOL5050_1 μL	Yes	ETAC / TOL	100.0
ETAC_TOL5050_2.5 μL	Yes	ETAC / TOL	100.0
ETAC_TOL5050_7.5 μL	Yes	ETAC / TOL	100.0
ETAC_TOL7030_1 μL	Yes	ETAC / TOL	100.0
ETAC_TOL7030_2.5 μL	Yes	ETAC / TOL	100.0
ETAC_TOL7030_7.5 μL	Yes	ETAC / TOL	100.0
TOL_ETOH3070_1 μL	Yes	ETAC / TOL	100.0
TOL_ETOH3070_2.5 μL	Yes	ETAC / TOL	100.0
TOL_ETOH3070_7.5 μL	Yes	TOL / ETOH	100.0
TOL_ETOH5050_1 μL	Yes	ETAC / TOL	100.0
TOL_ETOH5050_2.5 μL	Yes	TOL / ETOH	100.0
TOL_ETOH5050_7.5 μL	Yes	TOL / ETOH	100.0
TOL_ETOH7030_1μL	Yes	TOL / ETOH	81.1
TOL_ETOH7030_2.5 μL	Yes	TOL / ETOH	100.0
TOL_ETOH7030_7.5 μL	Yes	TOL / ETOH	100.0

Table 4.4: Identification results of the DFA for binary solvents validation data set. (ETAC: Ethyl acetate, ETOH: Ethyl alcohol, TOL: Toluene)

Code	ETAC:ETOH	ETAC:TOL	TOL:ETOH	% Correct Identification
ETAC:ETOH	9	0	0	**100**
ETAC:TOL	0	8	1	**88**
TOL : ETOH	0	3	6	**66**

4.3 Quantification of the Single Solvents

Figure 4.11 shows a typical PLS calibration curve which was used to predict the toluene concentrations. When constructing the PLS calibration curves, pre-determined GC area response values were used as a concentration value. In this typical calibration curve, the correlation coefficient was found to be 0.9787. The correlation coefficient between experimental and expected values is the evidence of how well the new model performed. In general, if the correlation coefficient is close to one, which indicates a perfect fit, the new model created can correctly predict the concentration. First, the PLS model was constructed by using training data sets, then it was validated by using validation data dataset (Figure 4.12), using the partially leave-one-out method (only one dataset, 5µl) (Figure 4.13), and running blind samples (unknown samples, 2.5µl) (Figure 4.14). The detailed experimental and predicted area response values for single solvents are tabulated in Appendix D.

Table 4.8 summarizes the correlation coefficient values between experimental and predicted area responses obtained from validation methods for single solvents. As can be seen from the results, we obtained correlation coefficient

values from **0.90** to **0.98** which shows there is a good fit between the concentration predicted by e-nose and the concentrations determined by GC. Therefore, the e-nose can be considered to provide accurate information on the concentration of residual single solvents in the LDPE films.

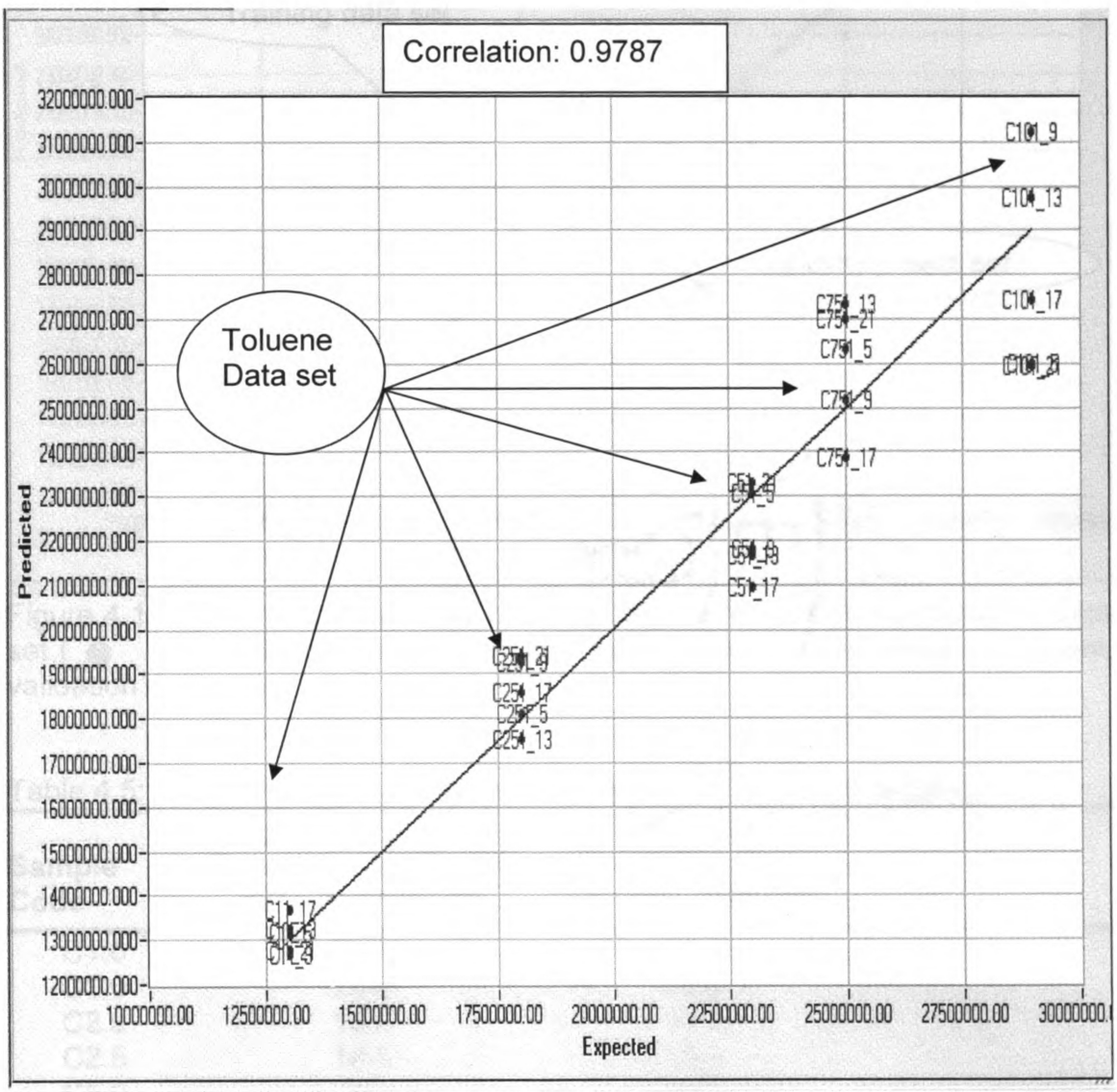

Figure 4.11: A typical PLS plot of the toluene samples (5 concentration - 5 replicates)

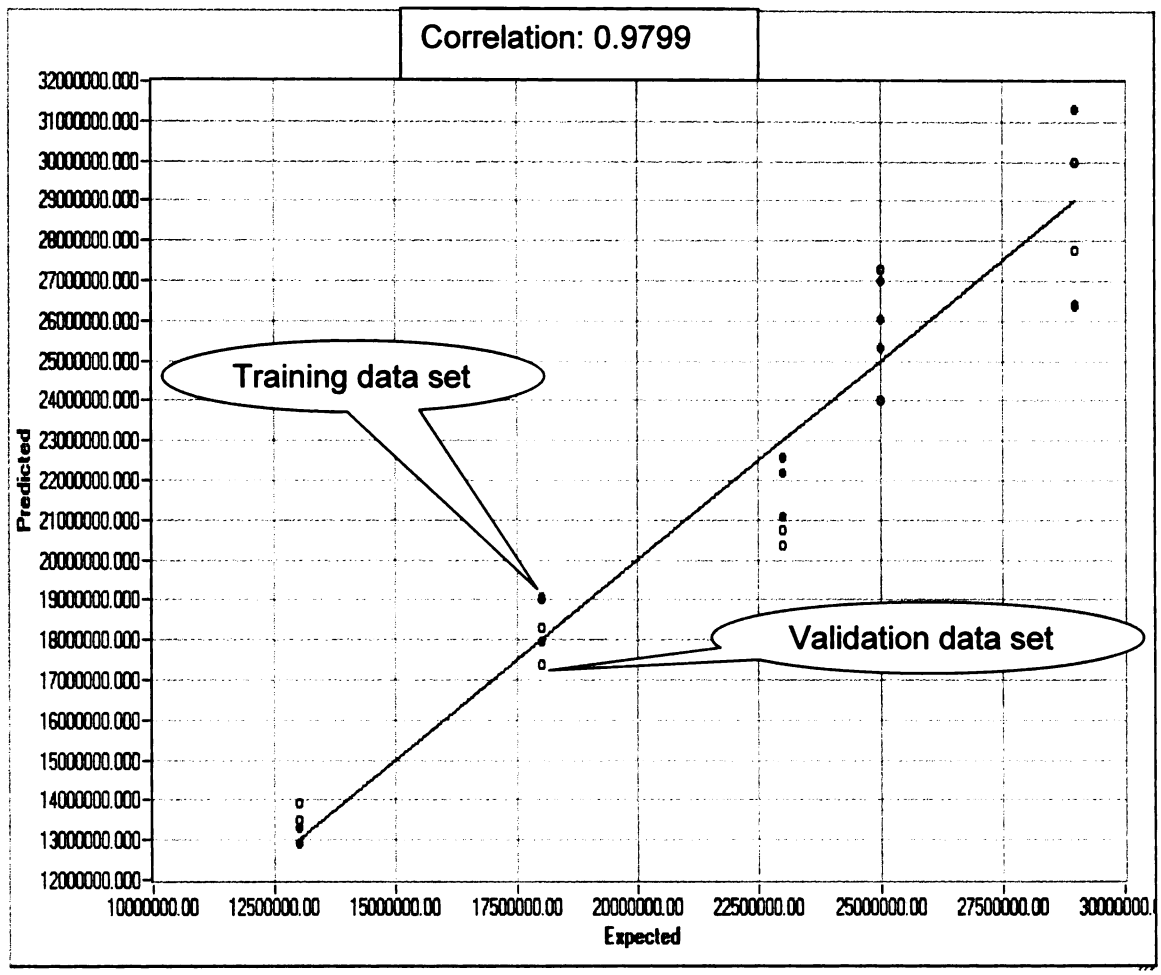

Figure 4.12: The PLS pot of toluene training data set validated by validation data set (● the filled circles represent training data set, ○ open circles represent, validation data set)

Table 4.5: Predicted values for validation data set (for toluene samples)

Sample Code	Experimental Area Response (Average) µV*sec, x10E+06	Predicted Area Response µV*sec, x10E+06
C1.0	13.0	13.4
C1.0	13.0	13.9
C2.5	18.0	17.4
C2.5	18.0	18.2
C5.0	23	20.7
C5.0	23	20.3
C7.5	25	27.2
C7.5	25	24.0
C10	29	29.9
C10	29	27.7

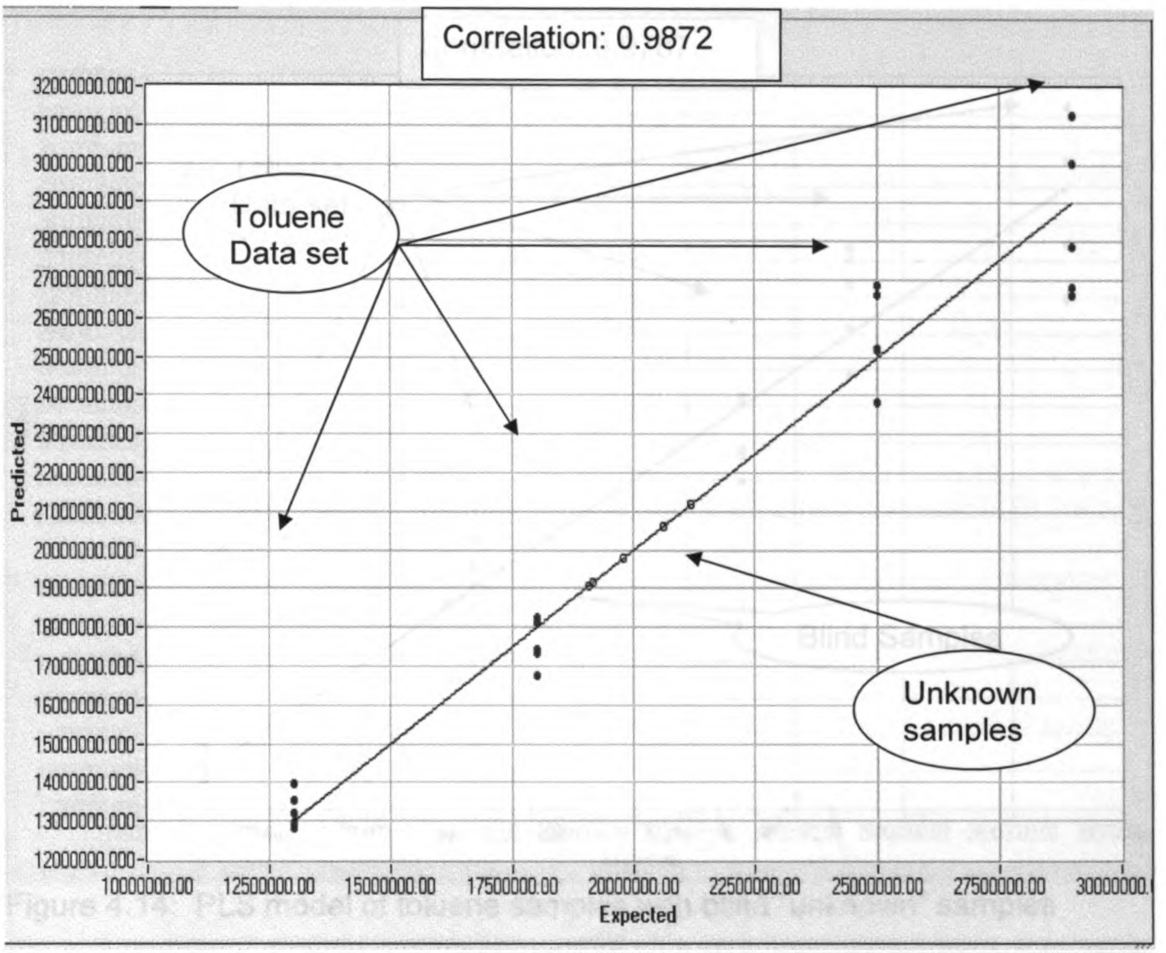

Figure 4.13: PLS plot of toluene samples constructed by leave-one-out method (samples without 5.0 µl), then unknown samples (5.0 µl) were projected onto the model.

Table 4.6: Predicted values for the unknown toluene samples (5.0 µl)

Sample Code	Experimental Area Response (Average) µV*sec, x10E+06±1.1*	Predicted Area Response µV*sec, x10E+06
C5.0	23.0	19.0
C5.0	23.0	19.0
C5.0	23.0	21.1
C5.0	23.0	20.6
C5.0	23.0	19.7
		AVERAGE 19.9
		STDEV. : 0.9

*Mean value x 10E+06 ± Standard deviation (three replicates)

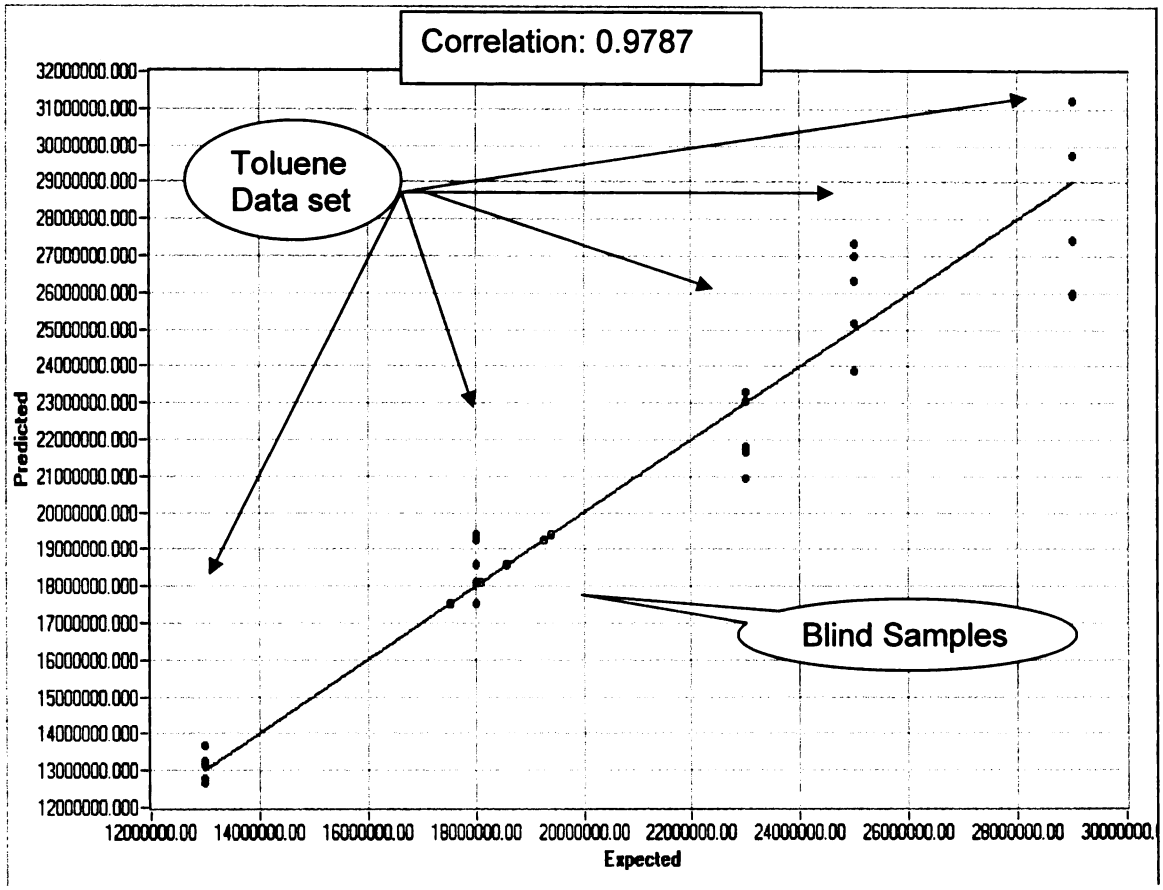

Figure 4.14: PLS model of toluene samples with blind "unknown" samples

● the filled circles represent toluene data set, ○ the open circles represent blind "unknown" samples

Table 4.7: Predicted values for the blind "unknown "toluene samples (2.5 µl)

Sample Code	Experimental Area Response (Average) µV*sec, x10E+06±1.3*	Predicted Area Response µV*sec, x10E+06
C2.5	18.0	17.5
C2.5	18.0	18.5
C2.5	18.0	19.4
C2.5	18.0	18.1
C2.5	18.0	19.2
	AVERAGE	18.5
	STDEV. :	0.7

*Mean value x 10E+06 ± Standard deviation (three replicates)

Table 4.8: Correlation coefficient values obtained from all validation methods for single solvents.

	Correlation Coefficient		
	Using all data sets	**Using training dataset**	**Using leave one data set out (5µl)**
ETAC	0.90	0.90	0.94
ETOH	0.94	0.95	0.95
TOL	0.97	0.97	0.98

4.4 Quantification of the Binary Solvents

Figure 4.15 illustrates an example of a typical PLS plot for TOL/ETOH training sets at 1 µL injection amount. The correlation coefficients between experimental and predicted values at varying injection amounts for binary solvent mixtures were found to be between 0.84 and 0.99 (Table 4.9 and 4.10). The PLS analysis results showed that the electronic nose can be used satisfactorily in quantitative analysis of binary solvents.

These almost perfect correlation coefficient values obtained from the model for single and binary solvents can be used satisfactorily in quantitative analysis. Moreover, if this new method is capable of predicting the concentrations, even though there is a poor identification/classification between mixtures, it would be possible to quantify the total residual solvents in the films without identifying/classifying them. This would bring a great advantage in quality control of packaging materials.

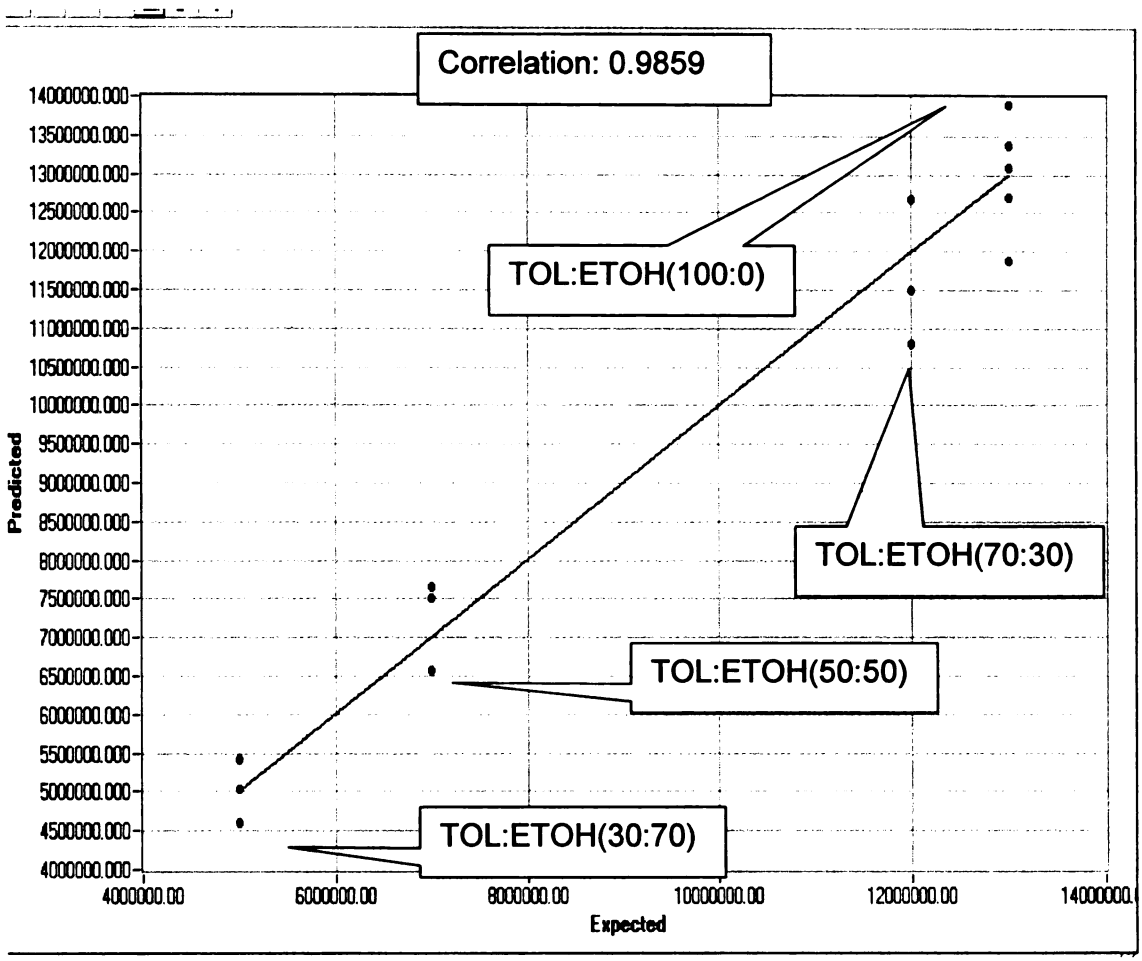

Figure 4.15: A typical PLS plot of TOL:ETOH data sets at 1 µL injection amount.

Table 4.9 : Summary of the correlation coefficient values obtained from the PLS calibration curves for binary solvents.

	Correlation Coefficient		
	1.0 µL	**2.5 µL**	**7.5 µL**
ETAC : ETOH 30:70, 50:50, 70:30, 100:0	0.91	0.92	0.95
ETAC : TOL 30:70, 50:50, 70:30, 100:0	0.89	0.96	0.84
TOL : ETOH 30:70, 50:50, 70:30, 100:0	0.98	0.96	0.96

Table 4.10 : Summary of the correlation coefficient values obtained from the PLS calibration curves for binary solvents.

	Correlation Coefficient		
	ETAC:ETOH	**ETAC:TOL**	**TOL:ETOH**
30:70 1.0, 2.5, 7.5 µl	0.99	0.98	0.99
50:50 1.0, 2.5, 7.5 µl	0.92	0.98	0.99
70:30 1.0, 2.5, 7.5 µl	0.95	0.98	0.98

5. CONCLUSIONS and RECOMMENDATIONS

A novel electronic nose method for assessing the residual solvents in low density polyethylene has been established. The proposed method is very useful for identifying and quantifying the residual solvents. The method presented is also simple, quick and reliable in predicting the total amount of residual VOCs present in low density polyethylene and thus useful for controlling the quality of the process.

It has been found that the electronic nose with the proposed method is capable of providing, for single and binary mixtures, quantitative analyses of residual solvents and can also distinguish between similar types of solvents. This is supported by high correlation coefficient values obtained in PLS analysis.

Further investigation is required to assess the effectiveness of the proposed method for identification and quantification of different binary and ternary mixtures of other VOCs. Further research could also involve the adaptation of this method into a quality control laboratory.

In recent years, with the introduction of new technologies such as biodegradable polymers, water-based, UV, and EB curable printing inks, the sources of off-odor started diversifying in the polymer and printing industry. The methods and residual solvent levels based on solvent-based inks, coatings and adhesives may not be applicable to these new technologies. Therefore, the electronic nose could also be used to establish standards for low odor with these new technologies.

APPENDICES

APPENDIX A

Table A.1 : Properties of the representative solvents (Wypych, 2001)

	ALCOHOLS	ESTERS	AROMATIC HYDROCARBONS
	Ethyl Alcohol	Ethyl Acetate	Toluene
Formula	C_2H_5OH	$CH_3COOC_2H_5$	$C_6H_5CH_3$
Density (g/cm ^{3})	0.789	0.901	0.867
Molecular Weight (g/mol)	46.1	88.1	92.1
Evaporation Rate (BuAc=1)	3.2	6.2	2.1
Boiling Point (° C)	78.3	77.2	110.8
Vapor Pressure (mm Hg, 20 °C)	44	73	21
Polarity Index	5.2	4.3	2.3
Miscibility Number	14	19	23

APPENDIX B

GC Analysis Conditions

Gas chromatographic analysis was performed using an HP 6890 (Hewlett-Packard, Avondale, PA) gas chromatograph, equipped with flame ionization detector (FID) and interfaced with Empower-Waters software. Gas chromatographic conditions used for single and binary solvent mixtures were as follows:

Column : Supelcowax 10 (Supelco Inc., Bellefonte, PA)
(60 m, 0.25 mm I.D., 0.25µm film thickness)

Carrier gas : Helium at 30ml/min

Temperature : Injector temperature – 250 °C, Detector temperature – 250 °C
Initial oven temperature- 40 °C isothermal
Initial time –10 min

First, 10 ml headspace vials were prepared using the method described in section 3.3.2. Second, the vials were heated in the oven at 60 °C for 20 min in order to equilibrate the solvent in the headspace of the vial with the sample. Then, a 100 µl portion of headspace created in the vial was injected manually into the gas chromatograph using a gas tight syringe. Since the solvent concentration in the headspace is a function of the concentration in the film, the recorded area response values are also proportional to the solvent concentration in the film samples. Therefore, all recorded area response values were used to build calibration curves for the e-nose analysis.

APPENDIX C

Outlier Detection

The outlier detection and rejection from the data set was one of the most vexing issues in this study. But the time spent for this part lead us to build a concrete model. First, it was necessary to have a valid reason for rejecting the point from the data set. For this purpose, two methods were used to find outliers.

1) Using PCA (Alpha MOS Fox 3000, Manual, 2001):

-Perform the group labeling in a way that repeats of each individual sample are clustered together.

-Build the PCA.

-Compare the cluster shape of all the groups.

The cluster shape must be quite similar, otherwise there is a good chance of having one or several outliers in the dataset.

2) Using sensor responses

By analyzing the sensor profiles, it can be visually seen if there is a significant difference between the replicates of each sample for each sensor.

APPENDIX D

Experimental and Predicted Area Response Values for Solvents

The following tables show the experimental and predicted area response values obtained from using three validation methods for ethyl acetate and ethyl alcohol.

Table D.1: Experimental and predicted values for ethyl acetate samples.

	Using Training Data Set	
Sample Code	Experimental Area Response (Average) µV*sec, x10E+06	Predicted Area Response µV*sec, x10E+06
A1.0	21.0	19.5
A1.0	21.0	21.6
A2.5	24.0	27.3
A2.5	24.0	27.4
A5.0	27.0	24.1
A5.0	27.0	26.0
A7.5	31.0	32.7
A7.5	31.0	33.0
A10.0	34.0	32.1
A10.0	34.0	33.0

Table D.2: Experimental and predicted values for ethyl alcohol samples.

	Using Training Data Set	
Sample Code	Experimental Area Response (Average) µV*sec, x10E+06	Predicted Area Response µV*sec, x10E+06
B1.0	9.0	8.9
B1.0	9.0	9.8
B2.5	10.0	9.5
B2.5	10.0	10.3
B5.0	13.0	11.3
B5.0	13.0	16.6
B7.5	18.0	21.0
B7.5	18.0	16.9
B10.0	21.0	15.0
B10.0	21.0	16.8

Table D.3: Experimental and predicted values for "unknown" ethyl acetate samples (5µl)

	Using Leave One out Method	
Sample Code	Experimental Area Response (Average) µV*sec, x10E+06±0.7*	Predicted Area Response µV*sec, x10E+06
A5.0	27.0	26.3
A5.0	27.0	26.2
A5.0	27.0	26.4
A5.0	27.0	25.3
A5.0	27.0	25.7
	AVERAGE:	25.9
	STDEV. :	0.5

*Mean value x 10E+06 ± Standard deviation (three replicates)

Table D.4: Experimental and predicted values for "unknown" ethyl alcohol samples (5µl)

	Using Leave One out Method	
Sample Code	Experimental Area Response (Average) µV*sec, x10E+06±0.9*	Predicted Area Response µV*sec, x10E+06
B5.0	13.0	12.0
B5.0	13.0	12.5
B5.0	13.0	13.2
B5.0	13.0	13.2
B5.0	13.0	10.3
	AVERAGE:	12.2
	STDEV. :	1.1

*Mean value x 10E+06 ± Standard deviation (three replicates)

Table D.5: Experimental and predicted values for blind "unknown" ethyl acetate samples (2.5µl)

	Running Blind Samples	
Sample Code	Experimental Area Response (Average) µV*sec, x10E+06±0.9*	Predicted Area Response µV*sec, x10E+06
A2.5	24.0	24.1
A2.5	24.0	25.9
A2.5	24.0	24.8
A2.5	24.0	24.0
A2.5	24.0	26.8
	AVERAGE:	25.1
	STDEV. :	1.2

*Mean value x 10E+06 ± Standard deviation (three replicates)

Table D.6: Experimental and predicted values for blind "unknown" ethyl alcohol samples (2.5µl)

	Running Blind Samples	
Sample Code	Experimental Area Response (Average) µV*sec, x10E+06±0.5*	Predicted Area Response µV*sec, x10E+06
B2.5	10.0	9.9
B2.5	10.0	10.5
B2.5	10.0	9.6
B2.5	10.0	10.9
B2.5	10.0	11.6
	AVERAGE:	10.5
	STDEV. :	0.8

*Mean value x 10E+06 ± Standard deviation (three replicates)

BIBLIOGRAPHY

Alpha MOS Fox 3000 operating manual, Release Jan. 2001.

Apps, A.E. 1958. Printink ink technology. Leonard Hill Ltd. London, UK.

ASTM F151-86 Standard test method for residual solvents in flexible barrier films. Annual book of ASTM Standards. Philadelpia, PA: 15.9, pp. 1070-1074.

ASTM F1884-98 Standard test method for determining residual solvents in packaging films. Annual book of ASTM Standards. Philadelpia, PA: 15.9, pp. 1465-1468.

Begley, T.H. 1997. Methods and approaches used by FDA to evaluate the safety of food packaging materials. Food Additive and Contaminants. 14:6-7.

Benali, F.: Henry, J.: and Delaunay, Y. 1995. Electronic nose potentially utilization on packaged products. Olfaction and electronic nose, 2nd International Symposium, Toulouse.

Bohartier, C.; Vernat-Rossi, V.: Breysee, C.: and Theboult, J. 1995. Caracterisation d'un emballage defectueux par analyse de sa fraction volatile. Industries Alimenttaires at Agricoles. 122: 849-852.

Carmel, L.; Sever, N.; Lancet, D. and Harel, D. 2003. An enose algorithm for identifying chemicals and determining their concentration. Sensor and Actuators B 93:77-83.

Das, R. 2003. Development of electronic nose method for evaluation of HDPE data, correlated with organoleptic testing. Master of Science Thesis. Michigan State University, East Lansing, MI.

Delpha, C.; Siadat, M. and Lumbreras, M.2001. An electronic nose for discrimination of forane 134a and carbon dioxide in humidity control atmosphere. Sensor and Actuators B 78:49-56.

Ezquerro, O.; Pons, B. and Tena, M.T. 2003. Headspace solid-phase microextraction-gas chromatography-mas spectrometry applied to quality control in multilayer-packaging manufacture. Journal of Chromatography A, 1008:123-128.

Goodner, K.L.; Dreher, G.J. and Rouseff, R.L. 2001. The danger of creating false classifications due to noise in electronic nose and similar multivariate analyses. Sensor and Actuators B. 80:261-266.

Huber, M.; Ruiz, J. and Chastellain. 2002. Off-flavour release from packaging materials and its prevention: a food company's approach. Food Additives and Contaminants. 19:221-228.

Kolb, B. and Ettre, L. S. 1997. Static headspace-gas chromatography: theory and practice. Wiley-VCH, USA.

Lau, O.W. and Wong, S.K. 1995. Contamination in food from packaging material. Packaging Technology and Science. 8:271.

Leland, J.; Schieberle, P.; Buettner, A. and Acree, T. 2001. Gas chromatography-olfactometry. American Chemical Society, Washington, DC.

Lin, C. 1995, Permeability of organic vapors through a packaged confectionery product with a cold seal closure: theoretical and practical consideration. Master of Science Thesis. Michigan State University, East Lansing, MI.

Lopez-Rubio, A.; Cava, D.; Lagaron, J.M.; Catala, R. and Gavara R. 2003. Mass transfer properties of organic compounds through EVOH copolymers as a function of ethylene content and environmental humidity. 21st IAPRI Symposium, Valencia proceedings. 92-95.

Maneesin, P. 2001. GC-MS and electronic nose analysis on off-flavor components in HDPE containers and correlation with sensory evaluation. Doctor of Philosophy dissertation. Michigan State University, East Lansing, MI.

Pearce, T.C.; Schiffman,S.S.; Nagle, H.T. and Gardner, J.W. 2003. Handbook of Machine Olfaction. Wiley-VCH.

Robertson, G. 1993, Food packaging: Principles and practice. New York: Marcel Dekker, Inc. 623-600.

Savastano, D.2003. The packaging ink market. Inkworld Magazine.11(31): 45-51.

Schaller, E; Bosset, J.O., and Escher, F. 1998. 'Electronic Noses' and their application to food. Lebensmittel-Wissenschaft und technologie. 31:305-316.

Soroka, W. 1995. Fundamentals of packaging technology. Institute of Packaging Professionals, Heindon, Virginia.

Suman, M.; Ricci, C.; Dalcanale, E.; Bersellini, U. and Sensi, L. 2003. AOS: from study to quality control. Italia Imballagio. 4: 195-206.

Thompson, B. 1998. Printing materials: science and technology. PIRA International. Surrey, UK. 123-286.

Van Deventer, D. and Mallikarjunan, P. 2002. Comparative performance analysis of three electronic nose systems using different sensor technologies in odor analysis of retained solvents in printed packaging. Journal of Food Science. 67(8):3170-3183.

Vlasov, J. and Legnin, A. 1998. Non-selective chemical sensors in analytical chemistry: from 'electronic nose' to electronic tonque. Journal of Analytical Chemistry. 361:255-260.

Williams, C. 2001. Printing ink technology. Pira international Ltd. Surrey, UK. 120-230.

Wypych, G. 2001. Handbook of solvents. John Wiley and Sons Inc. New York. 1105-1450