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Rajarshi Das

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Susan E. Selke

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DEVELOPMENT OF ELECTRONIC NOSE METHOD FOR EVALUATION OF HDPE DATA, CORRELATED WITH ORGANOLEPTIC TESTING

By

Rajarshi Das

A THESIS

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ABSTRACT

DEVELOPMENT OF ELECTRONIC NOSE METHOD FOR EVALUATION OF HDPE DATA, CORRELATED WITH ORGANOLEPTIC TESTING

BY

Rajarshi Das

A standard method for analyzing food grade high density polyethylene (HDPE) resins was developed using the electronic nose (E-nose) system. Eight different HDPE resin grades were analyzed using the E-nose. The E-nose system with Principal Component Analysis, was found to be capable of discriminating between the resin grades. The resin samples were soaked in ultra-pure water at $40 \pm 2^{\circ}$ C for 1 week. Water samples stored in contact with the resins were organoleptically evaluated at different concentrations by untrained consumer sensory panels and the resins were ranked based on the degree of off-flavor perceived. The E-nose was used to correlate the sensory data and the sensor responses for the various resin grades, using multivariate statistical techniques.

A good correlation was obtained between the E-nose sensor responses and the human sensory analysis data, when the resins were analyzed using standardized experimental run conditions. The method is capable of predicting the quality of an unknown food grade HDPE resin sample, in terms of its possibility of producing an off-flavor in drinking water, which could be a result of migration of low molecular weight compounds from the polymer.

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INTRODUCTION

The use of polymeric materials in packaging has been increasing at a very fast pace. Polymers, in comparison to other materials, have proved to be highly useable and competitive as packaging materials because of many advantages such as durability, light weight, flexibility, and low cost, engineered mechanical properties, transparency, suitability for direct food contact and convenience (Downes et al., 1996).

Food is one of the most important applications for plastic packaging. Polymeric materials are widely used for food packaging. Developments and findings in the area of food packaging can be applied to many other products and systems, e.g. pharmaceutical, chemicals, and other consumer products. Polymeric packaging materials are not totally inert; hence there may be physical and chemical interactions with the food product, which play a decisive role in the selection of the packaging material. The nature of these interactions includes permeation of gases and vapors across the package, migration of package components and additives into the food, and sorption of food components. These interactions can give rise to odors and degradation reactions in both the food and the polymer.

One of the sources of off-flavor and off-odor in food is the transfer and migration of certain components from the packaging material. For example, drinking water stored in plastic containers is often found to have a faint waxy flavor. Water, unlike other food items, cannot mask the off-flavor that transfers from some polyethylene packaging materials. Such migration could be because of formation of carbonyl groups from overheated polyethylene, residual catalysts in the polymer resin or antioxidant additives in the resins (Brody, 1989). These off-flavors are a concern to both the food industry and consumers as they can affect the safety, organoleptic qualities, and nutritive values of the food products (Thompson et al., 1994). Therefore, the need for effective quality control procedures becomes more obvious and relevant to provide safe and quality food product.

The compounds responsible for off-flavors in the food have, in general, very low concentrations, which sometimes become difficult to detect even by sensitive analytical instruments. Sensory analysis by consumer and expert panels is extensively used to detect such off-flavors, in addition to being used for product development and batch quality control in the food and beverage industry (Schmitt and Tan, 2001). Such organoleptic study has its own limitations as it is highly subjective and lacks standardization. This is due to the fact that all individuals are not equally sensitive to taste and odor perception. Human subjects require repetitive training for each type of product and cannot work for long stretches of time (Hansen and Wiedemann, 1999).

Gas chromatography–mass spectroscopy (GC-MS), which involves separation of complex vapor mixtures into individual compounds, is one of the most common techniques used to detect such off-flavors. The GC-MS response can be ambiguous, since strong off-flavors might be generated by chemical compounds even at very low concentrations (below the detection limits of the instrument). It is usually difficult to correlate such data with human sensory analysis (Hansen and Wiedemann, 1999).

The electronic olfactory system, commonly called the electronic nose system (E-nose), is an instrument that is analogous to the human olfactory system. It generates olfactory response profiles for various aromatic components of a food product. The E-nose is being extensively used in major food, cosmetic, and packaging companies for applications such as quality control, spoilage detection, flavor quantification, and origin identification (Schmitt and Tan, 2001). The E-nose results are objective in nature and can predict human sensory response from physical measurements. This may make it a more reliable tool than the human sensory panel in some applications and it minimizes dependence on subjective sensory panel tests for product evaluation (Hansen and Wiedemann, 1999). Electronic nose systems are used in the packaging industry to detect residual solvents in flexible packages that are released from printing inks, coatings, and adhesives; residual catalysts and antioxidants in plastic resins; organic volatiles formed in a polymer during package fabrication; and organoleptic changes in the product/package system.

The area of focus in this study is food-grade high density polyethylene (HDPE) resin, which is one of the most versatile polymers for packaging applications. These polymeric materials are used for drinking water pipeline manufacturing in addition to manufacture of blow molded food containers. In both cases, low residual organic compounds must be present in the HDPE pellets, which can otherwise be a potential cause of off-flavor in drinking water. Quality control of these materials can be quite difficult as only a few HDPE pellet grades have residual organic compounds that are likely to cause off-flavor in drinking water (Schmitt and Tan, 2001).

The specific objectives of this study are:

1. To develop a standard method for evaluating food grade HDPE resins using the electronic nose.
2. To correlate electronic nose results with sensory panel data for water off-flavor that is currently being used for the purpose.
3. To understand the experimental and statistical techniques and explore the potential of the electronic nose as a quality control tool for a variety of packaging applications.

This experimental method may eventually replace current sensory evaluation techniques, with a simpler qualitative and quantitative objective technique, offering better reliability and reproducibility of results and faster operation.

CHAPTER I

LITERATURE REVIEW

Polymers as packaging materials

There has been tremendous growth in the development and design of various packaging materials in the recent past, for a variety of applications. There have been adaptations of many traditional packaging materials, e.g. paper, metal, and glass. A major contributor to this growth has been the development and use of plastic packaging materials. The flexible plastic packages may be composed of a single polymeric material or a blend of more than one polymer or a multi-layered laminated structure, composed of multiple components. Common flexible packaging materials include polyethylene, polypropylene, polyester, polyamide, cellophane, ethylene vinyl acetate (EVA), polyethylene terephthalate (PET), polystyrene, polyvinyl chloride, polyvinylidene chloride, and acrylonitrile (Risch, 1988).

Food packaging is one of the major applications for such polymeric packaging materials. Food packages can be in the form of single layered extruded films, blow-molded bottles, and multi-layered laminated structures, depending on the degree of protection required from environmental, microbial, and physical damage of the product. As there have been remarkable improvements in the area of food package development, there has also been a concern about interaction of plastic packaging materials and foods. One of the major areas of concerns related to polymeric packages has been the presence of compounds in toxicologically insignificant amounts, but at levels affecting the flavor (aroma/taste) of the packaged food. The concern is both from a consumer standpoint and an industry perspective. The flavor balance in the food may be disrupted in three ways – absorption of components contributing to the desired food flavor by the packaging material (subtraction), chemical reaction of food with the package components (reaction) or release of compounds from the package into the food product (addition). Addition is the most common phenomenon for causing off-flavor in the packaged food (Kim-Kang, 1990). It is usually difficult to trace the source of off-odors and flavors in food, primarily due to the fact that most of the compounds that are responsible for such off-flavors have very low detection thresholds, even lower than the detection limits of the analytical instruments available. Although such odor-active compounds may not pose any health risk, they may cause concern in the consumer's mind about possible product contamination (Risch, 1988).

Drinking water, which is considered to be a food model (Cabral et al., 1977), has a very subtle taste and can be affected by off-flavors from packaging materials very easily. Such off-flavors and odors can be due to migration of specific compounds from drinking water bottles made of high-density polyethylene (HDPE), PET or PVC. A similar problem can be encountered when plastic pipes (HDPE or PVC) are used for domestic water supply (Skjevrak et al., 2003).

Interaction between plastics and food materials

As discussed earlier, plastic packaging materials are widely used for food products due to many advantages. However they are not totally inert; hence there may be physical and chemical interactions with the food product. There are several different types of reactions that can occur, including scalping (sorption), permeation, and migration. Scalping is the loss of a flavor into the packaging material. Such a phenomenon can also lead to damage to the package, e.g. increase in movement of gases and water vapor across the package and deterioration of physical characteristics and performance of the package. Migration is the movement of components of the packaging material into the food product, resulting in contamination of the product and potentially an undesirable off-flavor. Permeation of flavors and gases through the packaging materials can result in change of flavor profile and loss of flavor intensity of the food product, over time (Risch, 2000). Food-package interaction may also include a chemical change in the food product, the package, or both, thereby leading to degradation of the food or the package.

Theory of migration

The migration of low molecular weight compounds from the packaging material, residual monomers and oligomers, residual solvents from printing inks, adhesives, coatings, breakdown products of polymers and additives, are primarily responsible for causing off-flavor and off-odor in food products.

As explained by Kim-Kang (1990), the mechanism by which migration of such low molecular compounds take place is based on the classic theory of the diffusion of gases, described by Fick's law. According to the law, the rate of transfer, R, of a gas passing perpendicularly through the unit area of a section is proportional to the concentration gradient through the section.

$$R = - D(C) [dC/dx] \tag{1}$$

Where D(C) is the diffusion coefficient in cm^2 /sec, D can be a function of the diffusant concentration, C is the concentration of the diffusant in mol/cm^3 and x is the thickness of the material in cm.

Kim-Kang (1990) also explained that the amount of package components that may migrate from the packaging material to the solid or liquid food depends on the physical and chemical properties of both the food and the polymer. The controlling factors for the degree of migration are the original concentration of migrants, the solubility at the contacting phase, the partition coefficient between the polymer and the contacting phase, temperature, time and morphology of the polymer matrix (Gilbert et al., 1980). The properties of the polymer that can affect migration include molecular weight, percent crystallinity, chain branching, density, and affinity for migrants (Shepherd, 1982). Kim-Kang (1990) further explained that the diffusion mechanism depends on the volatility of the migrants. The more volatile the components are, the higher is their concentration in the package headspace. Migration does not always require direct contact between the food and packaging material.

Ho et al. (1994) pointed out that there are three possible factors that influence the degree of off-odor due to release of specific compounds from the packaging material into the food, namely, odor threshold, molecular weight and polarity. The lower the sensory threshold, the more readily the odor can be detected, as in the case of aldehydes and ketones. The molecular weight of the migrants controls their volatility. The lower the molecular weight, the more volatile is the odor compound. This affects how rapidly the low molecular weight odor compounds can desorb from the polymer matrix to the gas phase. Polar odor-compounds have a greater tendency to desorb from the non-polar polymer matrix (Ho et al., 1994).

Katan (1980) developed a model to define factors affecting migration in the three phases: food, packaging material, and environment. The migration variables included in the model were temperature, time, specific gravity of plastic and solvent, original mass of migrant in plastic, mass of migrant transferred during a specified time, mass of plastic and solvent, area of contact, and geometry of the system.

Petrova et al. (1976) studied the possibility of using acrylonitrile-butadiene-styrene (ABS) plastics for food contact applications. Three different ABS plastics were tested and all three of them were found to impart some off-flavor to drinking water after 10 days contact due to migration of monomers, but no off-flavor was noticed after only 3 days. Water was found to have 0.008-0.019 mg/l of styrene and 0.022-0.057 mg/l of acrylonitrile, which was slightly higher than the permissible limits.

Desobry (2000) studied the interaction between fatty foods and packaging materials. It was observed that residual contaminants or microorganisms in processed packaging materials could migrate into food and alter its quality. A fatty food has high affinity to the chemical contaminants in the package due to its hydrophobic nature, leading to a potential safety problem of migration. The fat molecules were found to enter the packaging absorbent sites and activate contaminant migration. Such interactions were also found to modify the gas and water permeability of the packaging material.

Sharma et al. (1990) reported the leaching of film anti-oxidants, e.g. butylated hydroxyanisole and butylated hydroxytoluene, into refined peanut and sunflower oils stored in contact with anti-oxidant containing polyethylene films at 37 deg. C. The storage stability of the oil was affected by film oxygen barrier properties and the presence of antioxidants in the film.

Off-flavor from packaging material

Off-flavors in packaged foods, which are often related to the packaging materials, are causes of many customer complaints. An off-flavor or off-odor unfavorably changes the organoleptic properties of the food (Briston and Katan, 1974). Various sources of off-flavor or off-odor compounds have been identified, which primarily include residual monomers and oligomers, polymer volatiles and additives, residual solvent from printing inks, types of adhesives and coatings, and other factors like processing temperature, sealing temperature, sterilization and extrusion processes (Thompson et al., 1994). The problem of off-flavor in food has major economic repercussions, which include recalls from the market and compensation claims, lost consumer confidence and shattered brand image and trade relations (Huber et al., 2002).

Passy (1983) reported an off-flavor in a fruit beverage due to migration of certain components from an adhesive used for lamination of the packaging material structure, polyester/aluminum/polyethylene, and also due to solvent used in the printing inks. However very little contamination of dry powder containing dextrose was found when it was packaged in the same packaging material. Passy (1983) also reported an off-flavor problem in chocolate and lemon cream cookies packaged in polystyrene trays, wrapped with printed cellophane. The prime reason for such off-flavor was found to be due to styrene monomer migration into the cookies.

Potts et al. (1990) explained the impact on taste characteristics of heated apple juice and drinking water samples due to its interaction with low-density polyethylene and ionomer. It was observed that the taste performance of the polymers was associated with their processing conditions. An increase in melt temperature or extruder output was found to increase the degree of oxidation, thereby reducing taste properties. An increase in web speeds, causing less surface oxidation, led to better taste properties.

Heydanek (1977) reported a “piney-spruce” off-flavor in breakfast cereal, which migrated from the package inner liner and specifically from the resin used with microcrystalline wax to laminate two layers of kraft paper. This resin was vacuum distilled and analyzed by gas chromatography, which eventually showed nine peaks of "piney-spruce" off-odor.

Leong et al. (1992) investigated the development of off-flavor in milk packaged in polyethylene-coated paperboard cartons. Whole milk, low fat milk, skim milk, and water were used as samples for study, and were filled into polyethylene-coated cartons. The products were evaluated using a 10 member sensory panel. Packaging off-flavor was found to develop in the milk and water samples after 1 day storage, which did not increase significantly even after 3 days of storage. It was concluded that the off-flavor compounds, which migrated from the internal polyethylene (PE) coating, were formed due to oxidative changes on the PE surface, which were largely soluble in water and quite volatile. Interestingly, milk packaged in half-pint cartons was found to have more off-flavor than milk in quart or half-gallon cartons. Hence it was confirmed that off-flavor problems that occur due to migration from package components would increase with decrease in the container size, due to the higher surface area to volume ratio.

Off-flavor from polyethylene

As described in the earlier sections, packaging materials may contain components that may transfer into the packaged food product and can adversely affect product flavor characteristics.

The source of off-odor in polyethylene materials might be i) formation of carbonyl groups due to overheated polyethylene, which typically occurs during extrusion and package manufacturing processes; ii) residual catalysts in the polymer resins, which depends on the resin manufacturing process and polymer characteristics and iii) antioxidant additives in polyethylene resins, which prevent the development of oxidized odors but can also create their own off-odors (Brody, 1989). Catalysts and antioxidants can sometimes interact to generate off-odor compounds.

Polyolefins such as polyethylene are often processed at high temperatures in the presence of oxygen and high shear stress, which may eventually lead to oxidative and thermal degradation of the polymer. Usually, low-density polyethylene (LDPE) tends to degrade to shorter chain hydrocarbons at temperature greater than 300°C and then further undergoes oxidation to form a variety of low molecular weight oxidation products such as aldehydes, ketones and acids (Hoff and Jacobsson, 1981; Kim-Kang, 1990). Such products of thermo-oxidative reactions in polyolefins can develop adverse flavors in the food product (Kim-Kang, 1990).

Bravo et al. (1992) collected volatiles from thermal oxidation of polyethylene and analyzed them by a gas chromatography/olfactometry technique. Fourteen odor-active compounds were detected, mainly saturated and unsaturated aldehydes and ketones, which were primarily responsible for off-odor associated with thermo-oxidation of PE. About 46% of the odor-active compounds detected from oxidized polyethylene were hexanal, 1-hepten-3-one, 1-octen-3-one, octanal, 1-nonen-3-one, nonanal, trans-2-nonenal, and diacetyl. The overall odor was termed as "waxlike".

In a similar study, Hoff and Jacobsson (1981) identified 44 compounds resulting from thermo-oxidative degradation of polyethylene between the temperatures of 264 – 289° C, using GC-MS analysis. These compounds were mainly hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, cyclic esters, and hydroxy-carboxylic acids. Out of all the compounds identified, fatty acids and aldehydes were predominant.

Ho and Yam (1999) reported the effect of vitamin E formulation in HDPE resin pellets on off-odor release. An antioxidant formulation of vitamin E, glycerol, polyethylene glycol-400 (PEG-400), and glyceryl monocaprylate/caprylate (GMC) was used for the study. Off-odor release from the resin pellets was evaluated using a sensory panel and GC/MS technique. The results confirmed that GMC was the main off-odor contributor.

Yam et al. (1996) studied the effects of three types of HDPE resins (A, B, and C) and three antioxidants (vitamin E, Irganox 1010, and BHT) on the release of off-flavor from blow-molded HDPE bottles, using sensory evaluation and GC/MS analysis. The sensory results confirmed that off-flavor intensity was influenced by both resin type and antioxidant. The GC/MS study identified more than 60 volatile compounds released from the bottles, which belonged to the groups of n-alkane, 1-alkene, aldehyde, ketone, phenolic, olefin, and paraffin. The aldehydes and ketones were found to have very low odor thresholds. Bottles made with Resin A, which had Vitamin E as the antioxidant, yielded the least off-flavor compared to the other two bottles made with Resins B and C. This was primarily due to the fact that the Resin A bottle yielded less aldehydes and ketones than the other two.

Fauconnier et al. (2001) developed a mathematical model for migration of odor components from HDPE into hexane, ethanol, lemon terpenes, and their emulsions, which are concentrated solutions used as food flavorings. Analysis indicated the presence of 2,4-bis(1,1-dimethylethyl)phenol in all the liquid solutions at all temperatures, which was probably a degradation compound of the antioxidant in the polymer.

Off-flavor problems in drinking water

Off-flavor in drinking water is a very common problem, both in cases of bottled water and domestic water transported in plastic pipes. The off-flavor in water is usually attributed to the plastic aftertaste, which is reportedly caused by migration of low molecular weight compounds and degradation products from the plastic.

Taste and odor complaints from consumers are a major problem for suppliers of drinking water. Small traces of chemicals, which could be naturally present in water or produced during water treatment or even leach out from the package, can alter the organoleptic properties of drinking water (Young et al., 1995). Brody (1989) reported that water, which has practically no aroma, cannot mask the faint waxy or burnt odor that transfers from polyethylene containers.

Fayad et al. (1997) studied the migration of vinyl chloride monomer and plasticizer migration from polyvinyl chloride (PVC) packaging material into bottled drinking water. It was reported that concentration of vinyl chloride monomer (VCM) in various brands of bottled water was less than 0.6 ppb (parts per billion), which is far below the 2 ppb maximum concentration limit set by the US regulatory body. However, the GC-MS analysis of the bottled water sample revealed the presence of several volatile and semi-volatile organic compounds, after the bottled water was exposed to sunlight. Dichloroacetic acid and 2,3-dichloro-1-propanol were the volatile compounds identified. In addition, the presence of benzene was confirmed in some bottled-water samples. Di-n-octyl adipate and bis(2-ethylhexyl) phthalate, which are widely used plasticizers for PVC, were the major semi-volatile organic compounds identified. Factors affecting migration were found to be the storage time, temperature, and exposure to sunlight.

Solin et al. (1988) studied the effects on the taste of drinking water stored in PVC, HDPE, polycarbonate, and polyethylene terephthalate (PET) bottles at room and elevated temperature (120° F), for 4 weeks. Water stored in PVC bottles was reported to have the least off-flavor, followed by PET, polycarbonate, and HDPE.

Crompton (1979) reported an increase in pH and total solids in bottled water, which could be due to migration of polymeric residues, non-polymeric additives and adhesive compounds from the plastic package.

Calvosa et al. (1994) analyzed the taste quality of drinking water samples stored in low-density polyethylene (LDPE) containers, which were exposed to direct sunlight for 2 weeks. GC-MS analysis of the water samples revealed the presence of ketonic compounds, from the photo-decomposition of LDPE, in addition to 3,5-dimethoxybenzaldehyde, n-butyl phthalate and i-butyl phthalate, from the ink.

Off-flavor in drinking water is a problem with plastic pipes. The compounds causing off-flavors are mainly carbonyl compounds. HDPE has gained more acceptance as a material for drinking water pipe manufacture because of its favorable mechanical properties, ease of handling during manufacture, and low permeability to external contaminants (Villiberg at al., 1998).

Anselme et al. (1985) performed a study on the cause of an intense plastic taste and odor problem in drinking water transported using polyethylene pipes in southern Paris, France, in summer 1984. Analysis of the water samples from the pipe by GC-MS revealed the presence of polymer additives, e.g. lubricants, antioxidants, stabilizing agents, and polar compounds such as aldehydes. The primary causes of such organoleptic changes in the water were attributed to dissolution of polymer additives and oxidation of the interior surface of the pipe during extrusion, with subsequent release of polar compounds. The burnt plastic odor of the water was due to migration of butylated hydroxytoluene (BHT), a common antioxidant used during plastic pipe and bottle manufacture.

Brocca et al. (2002) reported various organic chemicals, which migrated from four different types of polyethylene (used commonly for pipeline manufacture) into drinking water. Most of the compounds detected had a basic common structure characterized by a phenolic ring typically substituted with alkyl groups in the 2 and 6 positions of the aromatic ring. The presence of some of these compounds was attributed to impurities or by-products in phenolic additives, which are typically used as antioxidants during pipeline manufacture. The presence of a few other compounds was attributed to degradation products from the polymer additives during the extrusion process at 200-250° C in the pipeline manufacturing process.

In a similar study, Skjevrak et al. (2002) analyzed the migration of volatile organic compounds from HDPE, cross-bonded polyethylene (PEX), and PVC pipes into drinking water, which eventually caused off-odor in water. A wide range of esters, aldehydes, ketones, aromatic hydrocarbons, and terpenoids were identified as migration products from the HDPE pipes. However the major source of off-odor in water flowing in HDPE pipe was attributed to leaching of 2,4-di-tert-butyl-phenol, which is a degradation product from the antioxidants used in pipeline manufacture. The leaching of phenolic antioxidants such as BHT and alkylbenzenes has also been reported as a significant cause of off-odor in drinking water. The predominating volatile organic compound in the water from PEX pipes was methyl-tert-butyl ether (MTBE), whose concentration was found to be higher than the permissible limits. MTBE was considered to be a probable cause of off-odors in the water sample. The organic compounds in the test water from PVC pipe included hexanal, octanal, nonanal, and decanal.

Analysis of off-flavor from packaging materials

As discussed in the earlier sections, the potential package-related cause of off-flavor in the food is the migration of residual monomers and oligomers, breakdown products of polymers and specific additives, and residual solvents from printing inks, adhesives, and coatings. This demands strict quality control by the package and polymer manufacturer, so that the taste and odor problems associated with leaching of volatile compounds from the package can be kept at a minimum.

It has been really difficult to evaluate taste and odor problems both subjectively and objectively. The situation becomes even more difficult when very low levels of odor-active compounds are present. Typically, sensory evaluation by human subjects is used to detect such off-flavor, as it is easier to detect some chemicals by subjective organoleptic evaluations, as they are present in levels far below the detection threshold of analytical instruments such as GC-MS, solid phase micro extraction, and E-nose. Determination of odor threshold and the concentration of the odor-compound is a very important step in aroma research. The concept of odor threshold is very useful in defining odor purity, describing intensity and odor quality and evaluating which of the components contributes to a characteristic aroma (Teranishi et al., 1991).

Hodgson et al. (2000) reviewed literature on volatile organic compounds that originate from polyethylene during its manufacture, processing, storage, and service life. It was reported that analysis of such volatile organic compounds and off-flavors associated with them was performed using methods such as sensory evaluation, chromatograph techniques and their associated sampling techniques, including the "hot-jar" method and dynamic headspace sampling, gas chromatograph-olfactory sensing, and artificial olfaction (electronic nose) technology.

Vom Bruck and Hammerschmidt (1977) used headspace gas chromatography to determine off-flavor compounds associated with packaging materials such as LDPE and polystyrene, which would alter the organoleptic properties of the food.

Kiritsakis et al. (2002) explained the various methods to perform flavor analysis of olive oil, which include GC-MS technique, aroma extract dilution analysis (AEDA), electronic olfaction technology (E-nose) and advanced methods such as nuclear magnetic resonance spectroscopy, fourier-transform infrared technique, differential scanning calorimetry, high performance liquid chromatography (HPLC) and solid phase micro extraction (SPME). These methods can also be used to study oil-package interaction and off-flavor analysis.

Sensory Evaluation

Sensory analysis is a formalized, structured and codified methodology used for evaluation of physical appearance and organoleptic qualities of a food product. The various sensory attributes of a food item are appearance, odor/aroma/fragrance, consistency and texture, and flavor (aromatics, texture, chemical feelings). However most of the attributes overlap with each other (Meilgaard et al., 1991).

In some cases, sensory analysis works better than instrumental analysis for determining off-flavors in food products, since some off-flavors can be detected by taste but cannot be effectively and accurately measured using analytical instruments. In general, sensory panels can detect off-flavors and off-odors present at much lower concentrations than can analytical techniques (Peled and Mannheim, 1977).

Linssen et al. (1991) evaluated a taint in water packed in test pouches made of LDPE-lined aluminum, using 48 sensory panelists. Eight descriptive attributes were used by the panel: metallic, synthetic, dry, rough, astringent, musty, sickly and penetrating. Fourteen panelists were used to judge intensities for these attributes on a visual analog scale. Factor analysis reduced the original data matrix to a 6 dimensional one. Synthetic and penetrating loaded high on one factor where as rough and astringent on another one.

Peled and Mannheim (1977) studied off-flavor in milk using sensory and GC techniques. It was reported that the organoleptic tests were more reliable than gas-chromatograph tests, in determining packaging off-flavors.

Olsen and Ashoor (1987) studied the impact on flavor, odor, and appearance of retail milk samples stored in 3.8 liter HDPE plastic containers and 1.9, 0.95, and 0.48 liter fiberboard containers and displayed under normal fluorescent light. 25 untrained sensory panelists were employed to detect any light induced off-flavor in milk. The riboflavin content was determined by the HPLC method. The results indicated that under typical production and storage conditions in the area, type and size of container, fat content, and season of production had no major damaging effects on flavor, odor, appearance, or riboflavin content of retail milk.

Adebiyi et al. (2002) used sensory analysis to evaluate the quality attributes of dry roasted peanuts which were processed in five different ways, packed in four different packaging materials, and stored under three different relative humidity conditions for 3 months at ambient temperature. Ten trained sensory panelists were employed to evaluate the color, taste, flavor, texture, crunchiness, and overall acceptability using a nine point hedonic scale. The sensory results indicated that there was no significant difference in color scores among all peanut samples. Salting was found to improve the taste, flavor, palatability, and overall acceptability of dry-roasted peanuts. However salting had no effect on the level of crunchiness and texture of the dry roasted peanuts.

Al-Bachir and Mehio (2001) conducted sensory evaluation to detect differences between irradiated and non-irradiated luncheon meat during an effort to study the effect of gamma irradiation on shelf life of luncheon meat. A consumer panel comprised of 20 subjects was employed to evaluate the taste and flavor of the meat and rank the samples on a 5-point scale. The sensory evaluation indicated that no significant differences were found between irradiated and non-irradiated samples in terms of taste and flavor.

Church and Parsons (2000) employed sensory evaluation techniques to study the quality of chicken breast and of sliced potatoes in cream, both immediately after cooking under vacuum (sous vide) and following subsequent chilling, chilled storage and reheating. Trained panels comprising of 25 subjects were employed and the quality of the food was evaluated using attribute scaling methods. Results revealed that sous vide significantly increased the flavor intensity of both products ($p<0.05$) and the juiciness and moistness of the chicken and potato respectively ($p<0.05$), compared to non-vacuum packed freshly cooked products.

Wheeler et al. (1999) employed a trained descriptive attribute sensory panel to evaluate the palatability of gamma irradiated vacuum-packaged frozen ground beef patties and the taste of hamburgers made with those patties. The trained panel evaluated grilled patties for ground beef aroma intensity, off-aroma, and off-flavor on 4-point scales (4 = intense; 1 = none) and ground beef flavor intensity, tenderness, and juiciness on 8-point scales (8 = extremely intense, tender, or juicy; 1 = extremely bland, tough, or dry). Control patties had more intense ($p<0.05$) ground beef aroma, less off-aroma, and more intense ground beef flavor than irradiated patties. Hamburgers made with patties treated with 4.5 kGy radiation were rated lower ($p<0.05$) in taste than hamburgers made with either control patties or those treated with 3.0 kGy radiation.

Okayasu and Naito (2001) employed sensory panels to evaluate the sensory characteristics of unclarified apple juice and to compare unclarified and clarified types. 140 consumers and 10 trained panelists evaluated 16 apple juice samples (4 clarified and 12 unclarified). It was difficult to predict consumer preference by regression models using trained panel results and analytical attributes.

Durst and Laperle (1990) employed a 12 member trained sensory panel to determine the presence of styrene off-flavor in apple juice stored in polystyrene containers. A standard triangle test method was used, where each panelist was presented with three glass samples of apple juice, comprised of two glass controls and one stored in plastic, or one control and two samples stored in plastic. The panelists were required to choose the odd sample and detect styrene related off-flavor. The sensory panel did not perceive a difference in flavor between juice packed in polystyrene containers and glass jars after 1 and 2 week storage times at 24° C. More than 50% panel members detected a styrene-like off-flavor after 4 weeks storage. A significant difference at 99% confidence level was found after a span of 8 weeks.

Sensory evaluation of drinking water

Drinking water is very sensitive to any off-flavor or odor, which can be due to any contamination from an external source or due to migration of certain compounds from the package into the water. Recently, there have been rapid developments in the area of powerful analytical techniques. However the human nose can still easily detect trace amounts of chemicals at levels many times lower than the analytical detection limits. Although many taste and odor assessments of drinking water have been conducted using sensory panels, such sensory data played up till now only a minor role in the management of the water treatment plant and understanding packaging requirements of water (Koster et al., 1981).

Young et al. (1995) used sensory evaluation to determine taste and odor threshold concentrations of 59 potential drinking water contaminants. These contaminants can be naturally present in raw water or can be introduced from industrial sources or during water treatment. The panelists included trained female subjects who ranged between 22 and 25 years of age and were above average in their basic sense of taste and odors. The subjects were not allowed to eat or drink or wear any kind of cosmetics or perfumes during the organoleptic evaluation, as those might interfere with the evaluation. The results indicated that there was no correlation between organoleptic effects of drinking water contaminants and their toxicity. It was found that chemicals with lowest taste and odor threshold values included chemicals such as geosmin, 2-methyl-isoborneol, and chlorinated phenols and anisoles.

Righi et al. (1999) performed a study on off-odor problems in non-carbonated mineral water packaged in 750 ml. disposable glass bottles and sealed with aluminum screw caps. The off-odor developed during storage of water in the glass bottle. A five member sensory panel evaluated a set of 120 samples. The water odor problems were attributed to screw caps contaminated with a Penicillium fungus.

Ho et al. (1994) evaluated the organoleptic properties of HDPE containers produced using Vitamin E, Irganox 1010, and BHT as antioxidants, using sensory evaluation of water. 32 untrained panelists were employed. A specified amount of water was filled in the HDPE containers and stored in controlled test conditions for 4 days. The taste of the water was evaluated by a duo-trio test. The odor of the water sample was judged by sniffing the headspace of the bottle. A 15 cm line scale was used to assign scores to the water samples based on the degree of off-flavor or off-odor present. "0" was assigned if there was no detectable odor and "15" was assigned if there was a strong off-flavor.

Instrumental analysis of off-flavor

Instrumental analysis of trace organic compounds in food requires very sensitive analytical instruments, which can detect volatile vapors at very low concentrations and have high discrimination capability. The most common instrumental methods used for detection and identification of unknown volatile compounds are gas chromatography – mass spectrometry (GC-MS), electron impact (EI); chemical ionization (CI); and gas chromatography – infrared spectroscopy (GC-IR) (Maneesin, 2001). Among these, gas chromatography – mass spectrometry (GC-MS) is the most widely used method to detect taste and odor compounds in food.

Steele at al. (1994) determined styrene levels in 12 different food commodities using analytical measurement techniques such as the dynamic heated headspace purge-and–trap extraction technique, which was followed by quantification using selected ion monitoring capillary gas chromatography/mass spectrometry.

Tombesi (2002) developed a method to detect the presence of butylated hydroxytoluene (BHT) in mineralized bottled drinking water, using solid-phase microextraction (SPME) and GC-MS. BHT is a common antioxidant used in bottle manufacture, which has a high chance of migration into the water sample.

Wyatt (1986) developed a dynamic headspace technique, to analyze the taste and odor compounds imparted from packaging materials. In this method, volatile aroma and flavor compounds were generated by heating the packaging material into a vapor stream, subsequently swept away by nitrogen gas and purged. The volatiles were then trapped by adsorbents and analyzed by GC-MS. The procedure was found to be rapid and reproducible, with a low detection limit and high precision.

Doust et al. (2003) studied the migration of organic compounds from polyethylene to packaged water. Liquid – liquid extraction and GC-MS were used to study the possible migration of certain organic compounds, such as oligomers, from polyethylene to packaged water. Primarily, tridecane, tetradecane, hexadecane, octadecane, and eicosane were detected in the polymer, using the analytical techniques, which was believed to alter the organoleptic properties of drinking water.

Giese (2000) pointed out that the classical analytical techniques such as GC-MS could separate, quantify, and identify individual volatile chemicals. However such techniques cannot tell if the component has an odor and it is often very difficult to correlate this data with the sensory evaluation data. Human sensory evaluation, as discussed earlier, is a powerful method, but it has limitations, such as it is time consuming and expensive. The sensory study conducted by trained human subjects is subjective, and illness and other factors can adversely affect their performance. Giese (2000) also explained that instruments like the electronic nose could be highly advantageous compared to other analytical instruments and sensory evaluation methods. The prime advantages of the electronic nose include rapid, real-time detection of volatiles, less preparation time, greater safety, and lower costs.

Electronic nose technology

The electronic nose is defined as an instrument comprised of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognizing simple or complex odors (Gardner and Barlett, 1993).

The basic mechanism of an electronic nose is to generate headspace over the sample being tested, present the headspace gas to the sensors, record the sensors' response, and analyze the data. Different types of sensors are commercially used in electronic noses, which include metal oxide sensors, conducting polymers, and quartz crystals. Metal oxide sensors are made from zinc or tin oxide. Such sensors are operated between two electrodes at high temperatures - 300° C. The aroma compound gets oxidized on the surface of the sensor and changes the resistance of the sensor. Conducting polymer sensors are obtained by electro-polymerization of a thin film of polymer across the gap between gold-plated electrodes. The electrical conductance of the film changes according to the odor compounds adsorbed on its surface. In the quartz crystal category, two different types of sensors are used. One is based on sensing the mass of the aroma compound absorbed into the stationary phase coated on the crystal surface. The adsorption changes the frequency of vibration of the crystal, due to change in mass. These sensors are called quartz microbalances. The second type of sensor is a surface acoustic wave device. It operates similarly to the quartz microbalance, apart from the fact that a surface wave is used to measure the absorbed quantity of aroma compound (Culter, 1999).

As reviewed by Schaller et al. (1998), there is another type of metal oxide semiconductor sensor used in electronic noses commercially, known as a metal oxide semiconductor field-effect transistor (MOSFET) sensor. A MOSFET sensor is comprised of three layers: a silicon semiconductor, a silicon oxide insulator, and a catalytic metal such as palladium, platinum, iridium or rhodium. The catalytic metal is also called the gate. In the MOSFET transistor, the gate and the drain contacts are shortcut. The applied voltage on the gate and drain contact creates an electrical field, which alters the conductivity of the transistor. Hence when polar odor compounds interact with the metal gate, the electric field is modified, which eventually modifies the current flowing through the sensor.

The electronic nose is an analytical instrument that can recognize flavors, odors, and volatile compounds. It has many advantages over the subjective sensory panel evaluation of odors and flavors as it eliminates the factor of fatigue, inconsistency, and high cost involved in human sensory analysis. An electronic nose is composed of a chemical sensing system such as a sensor array and a pattern recognition system. Each sensor is sensitive to a certain volatile compound and generates a signature or pattern characteristic of the vapor. Different chemicals can be presented to the sensor array, which can be used to build a database of signatures. Such a database can be used to train the pattern recognition system of the electronic nose (Giese, 2000).

Culter (1999) pointed out that analytical measurement technique such as GC-MS can detect individual components in a volatile vapor, but such components do not necessarily represent the combined sensory effect of the vapor. Moreover, the trained human subjects are not always available to perform a sensory analysis.

Schaller et al. (1998) pointed out that the electronic nose has been successfully used as a quality control tool to evaluate quality of various food products such as meat, grains, coffee, beer, mushroom, cheese, sugar, fish, blueberry, orange juice, cola, and alcoholic beverages. It is also being widely used to analyze off-flavors in food due to packaging.

Heinio and Ahvenainen (2002) used the E-nose to analyze the taints caused by pigments of printed solid boards. The objective of the experiment was to determine the effect of printing inks on the sensory properties of the packaging material, using the E-nose, which was correlated with human sensory evaluation and other headspace methods such as GC-MS. Twenty samples were studied, which included unprinted solid board, lacquered solid board, offset printed solid board with 14 different colors, and offset printed, lacquered solid boards with 4 colors. The E-nose was found to be very successful in discriminating the different board samples based on their coloring agents or lacquering. The results also indicated correlation with the off-flavor perceived during sensory evaluation.

Winquist et al. (1993) used the E-nose to study the quality of ground beef and pork and also estimate storage time in a refrigerator, based on the organoleptic property of the meat after storage. The electronic nose used consisted of a gas sensor array combined with a pattern recognition routine. Samples of ground beef and pork, stored in a refrigerator, were studied. The E-nose was successful in identifying the type and quality of meat.

Benedetti et al. (2002) explored the use of the electronic nose to study the shelf life of ripened Taleggio cheese packaged in paper. The electronic nose used for the study had an array of 10 MOSFET sensors and 12 MOS sensors. The E-nose was found to effectively classify and discriminate among cheese samples based on differences in their storage time and temperature. The different storage times and temperatures influenced the aroma characteristics of the cheese, which was sensed by 6 of the 22 sensors, which had good discrimination power.

Van Deventer and Mallikarjunan (2002) analyzed and compared the performance of three electronic nose systems as a quality control tool, used for detecting retained printing solvents in packaging. Three electronic nose systems were used, which had different sensor technologies – metal oxide semiconducting sensors, conducting polymer sensors, and quartz microbalance sensors. Each system was used to test 3 different film classes, with varying retained solvents. It was concluded that the E-nose with conducting polymer sensor technology had the highest discriminatory power. However, all the electronic noses were found to be capable of discriminating among the film samples at different levels of retained solvents.

Willing et al. (1998) used an electronic nose for measuring odors from paperboard, intended for packaging applications. Nine different paperboards from a wide range of board grades were analyzed in the electronic nose. The electronic nose was equipped with 10 MOSFET sensors, 4 Tagushi sensors, and 1 carbon dioxide sensor. The partial least squares regression (PLS) method was used to correlate electronic sensor responses with sensory panel descriptors. Some electronic sensor responses correlated well with a selected number of panel descriptors, while others did not fit with any panel descriptors.

Electronic nose technology is still in its development phase, both in respect to hardware and software development. It still has a few disadvantages. It cannot provide sufficient quantitative information for certain aroma differences (Harper, 2001). In addition, the electronic nose system is prone to sensor drift, which occurs due to aging and degradation of individual sensors. Drift results in gradual change in output over time without any significant change in input. Thus it hinders the reproducibility of the system. Calibration of sensors and sensor replacement after a fixed time interval can help in minimizing this problem (Maneesin, 2001). Moreover, the sensors are sensitive to moisture. Conducting polymer sensors are more sensitive to moisture than the metal oxide sensors, which can be minimized by using a filter and an air conditioning unit (Culter, 1999).

CHAPTER II

MATERIALS AND METHODS

This research was directed towards developing a standard experimental procedure for evaluating food grade HDPE resins using an electronic nose, correlated with the traditional sensory evaluation technique, for detecting off-flavor in drinking water. As a part of the procedure, the electronic nose system was used to analyze the degree of discrimination between eight different grades of HDPE resin. The experimental run conditions in the electronic nose that gave the highest degree of differentiation between the resin samples were standardized. Specific quantities of resin samples were soaked in ultra-pure water at 40 ± 2^{o} C for 1 week. Water samples stored in contact with the resins were evaluated for off-flavor by a human consumer sensory panel. The water samples were organoleptically evaluated at different concentrations and the resins were ranked based on the degree of off-flavor generation. Finally, the electronic nose was used to correlate the sensory data and the e-nose sensor responses for the various resin grades, using multivariate statistical techniques. The experimental design is summarized in Figure 1.

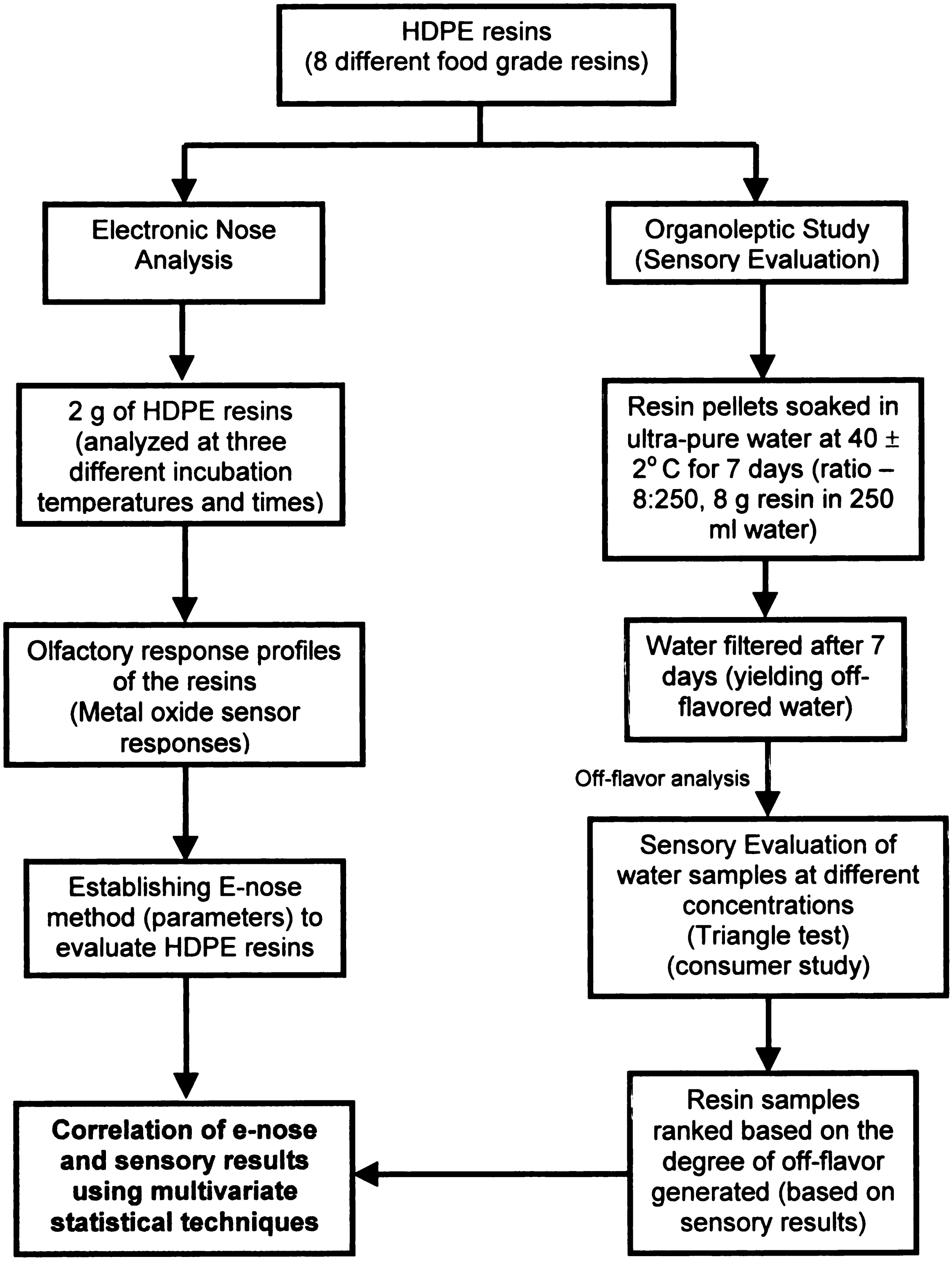

Figure 1 : Experimental Summary (E-nose evaluation of HDPE resins correlated with sensory results)

Electronic Nose System

The Fox 3000 electronic nose (E-nose) system (Alpha M.O.S. SA, Toulouse, France) was used in this study, which has three main components - Static Headspace Autosampler (HS100), Sensor Array System (Fox 3000), and controlling computer software (Fox 3000 software). Figure 2 shows the various components of the E-nose.

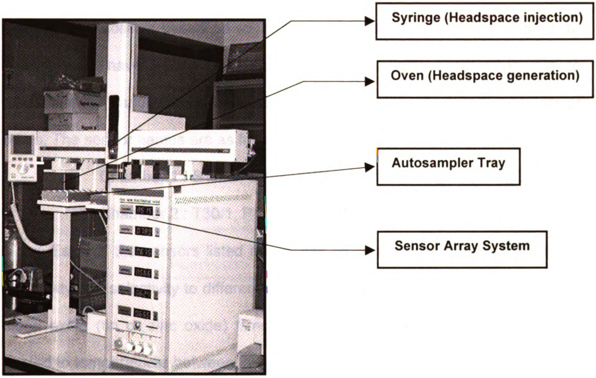

Figure 2 : Alpha MOS Fox 3000 E-nose system components

The static headspace autosampler generates the headspace (vapors) over the sample being tested. It includes a sample holding tray (capable of holding a maximum of 64 vials), an oven to heat the sample vial (10 or 20 ml) to the temperature required for headspace generation, and an agitator to facilitate homogeneous headspace generation. The temperature for heating the sample (incubation temperature) and the time of heating (incubation time) must be standardized and controlled for a specific sample, so that the same amount of sample vapors is generated each time. The quantity of sample loaded in each vial must also be standardized to ensure injection repeatability. The autosampler also has a gas syringe (1 to 5 ml) to collect headspace vapor and inject it into the sensor array system. The gas syringe temperature is maintained slightly above the sample temperature to avoid any condensation.

The E-nose is based on an array of 12 metal oxide sensors (Figure 3). The sensors have partial responses to specific volatile compounds due to reactions with various kinds of molecules and produce olfactory fingerprints of odors. The sensor names are as follows.

Chamber 1 : SY/LG, SY/G, SY/AA, SY/GH, SY/gCTI, SY/gCT

Chamber 2 : T30/1, P10/1, P10/2, P40/1, T70/2, PA2

Each of the sensors listed above has its own characteristics in terms of sensitivity and selectivity to different volatile compounds. The sensors have thick metal oxide (tin or zinc oxide) films deposited onto ceramic tubes, which are heated to temperatures between 300-500° C.

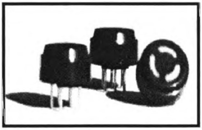

Figure 3 : Metal oxide sensor (Source : Alpha M.O.S. SA, Toulouse, France)

Figure 5 depicts the architecture of the gas array sensor system. Metal oxides are doped with various catalytic metals to shift the sensitivity and responsiveness of the sensors to particular chemical volatiles. The detection principle is based on conductivity measurements. The sensor adsorbs oxygen from the air on its metal oxide layer by trapping free electrons from n-type semiconductors, producing a highly resistive layer. This adsorbed oxygen is removed from the surface temporarily, in the presence of volatile reducing compounds, resulting in an increase of free electrons. This increases conductivity of the metal oxide film. The time-dependent electrical response due to change in conductivity of the sensor is interpreted as an olfactory fingerprint of an odor (Mielle, 1996).

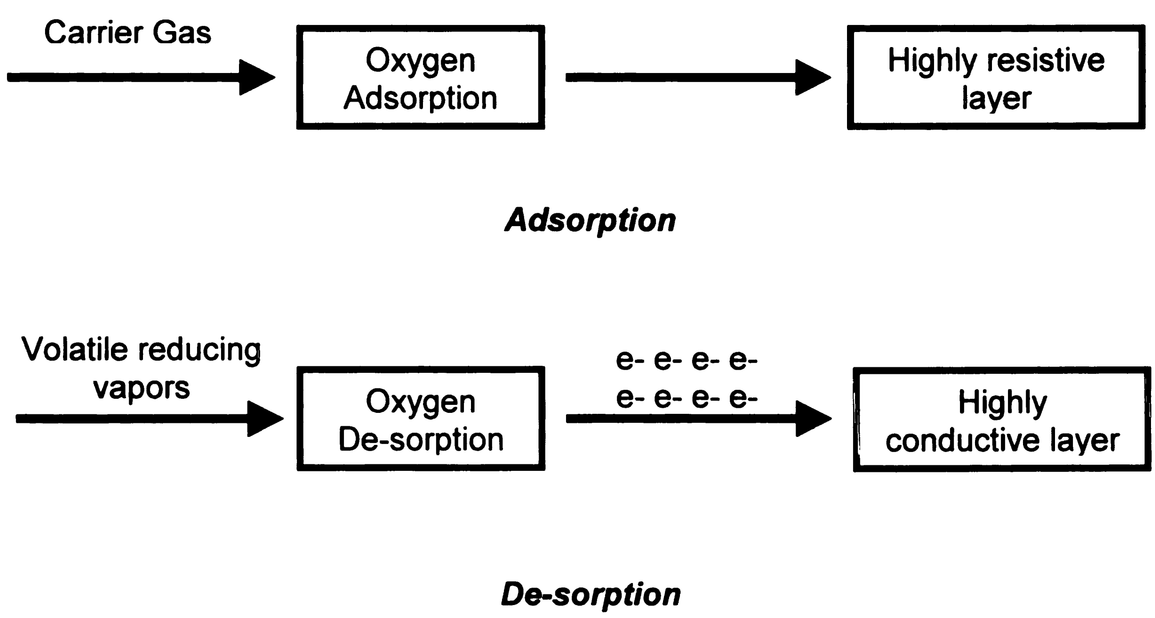

Figure 4 : Change in resistance of sensors due to action of reducing chemical vapors

These reactions with the chemical volatiles are influenced by parameters such as the carrier gas purity, operating temperature, carrier gas flow rate and humidity, which need to be carefully controlled for rapid response and recovery time. The sensors operate at high temperature to avoid interference from water.

Table 1 shows the responsiveness of various metal oxide sensors to a variety of chemical compounds, associated with different applications.

The Fox 3000 software package is used for data acquisition and processing in addition to driving the E-nose operational steps. The electrical response profiles obtained from the gas sensors are summarized in a data bank or library. Multivariate statistical data analysis methods such as Principal Component Analysis (PCA), Discriminant Function Analysis (DFA), Soft Independent Modeling of Class Analogy (SIMCA), Partial Least Squares (PLS), and Statistical Process Control (SPC) are used for sample group identification, discrimination, and sensory score correlation.

Table 1 : Metal oxide sensors used in Fox E-nose systems (Maneesin, 2001)

Description		Application	Metal Oxide Sensors			
			P Type	T Type	SX Type	SY Type
Non polar volatile	Hydrocarbon Methane and propane	Cooking, roasting of coffee, petro-chemical	P10/1 P10/2	T10/1 T10/4	SX13 SX13p SX14 SX14d SX15 SX42	SY/WM SY/CT
Hydrogenated Molecules	Hydrogen bonding Aldehydes	Milk industry, food freshness, animal rancid odors	P10/9 PA3	T10/9 TA3	SX21	
Organic Solvents	Polar compounds	Liquors, beers Alcoholic perfumes, fermentation	P30/1	T30/1	SX22	SY/WC
	Alcohols, Solvents		PA2	TA1		
Aromatic Compounds	Alcohol & aromatic compounds	Paint & polymer industry	P70/0 P70/1	T70/0-70/1 T70/2-70/3	SX23	SY/GC
		Smoke detection Hydrogen bonding	PA3			
Ammonia and sulphur	Amines and amine containing compounds & ammonia derivatives	Meat and fish freshness Environment	Under study	T50/3	SX24	SY/GA
	Sensor for sulphur	Environment, THT in butane	Under Study	T50/1	SX25	
Fluoride and Chloride	Sensor for fluorinated & chlorinated compounds, aldehydes	Environment packaging, TCA	P40/1 P40/2	T40/1 T40/2	SX30 SX31 SX32	SY/LG
Cooking control (food aroma & volatile	Alcohol compounds	Petrochemical		T70/2 T70/3	SX82	
	Food aroma and volatile	Natural aroma, coffee	P70/0 P70/1	T70/0 T70/1	SX83 SX83T	
Air quality control	Tobacco smoke and quality of air carburant vapor	Environment and applications in smoke detection	PA3	TA1 TA3	SX00 SX80 SX84	

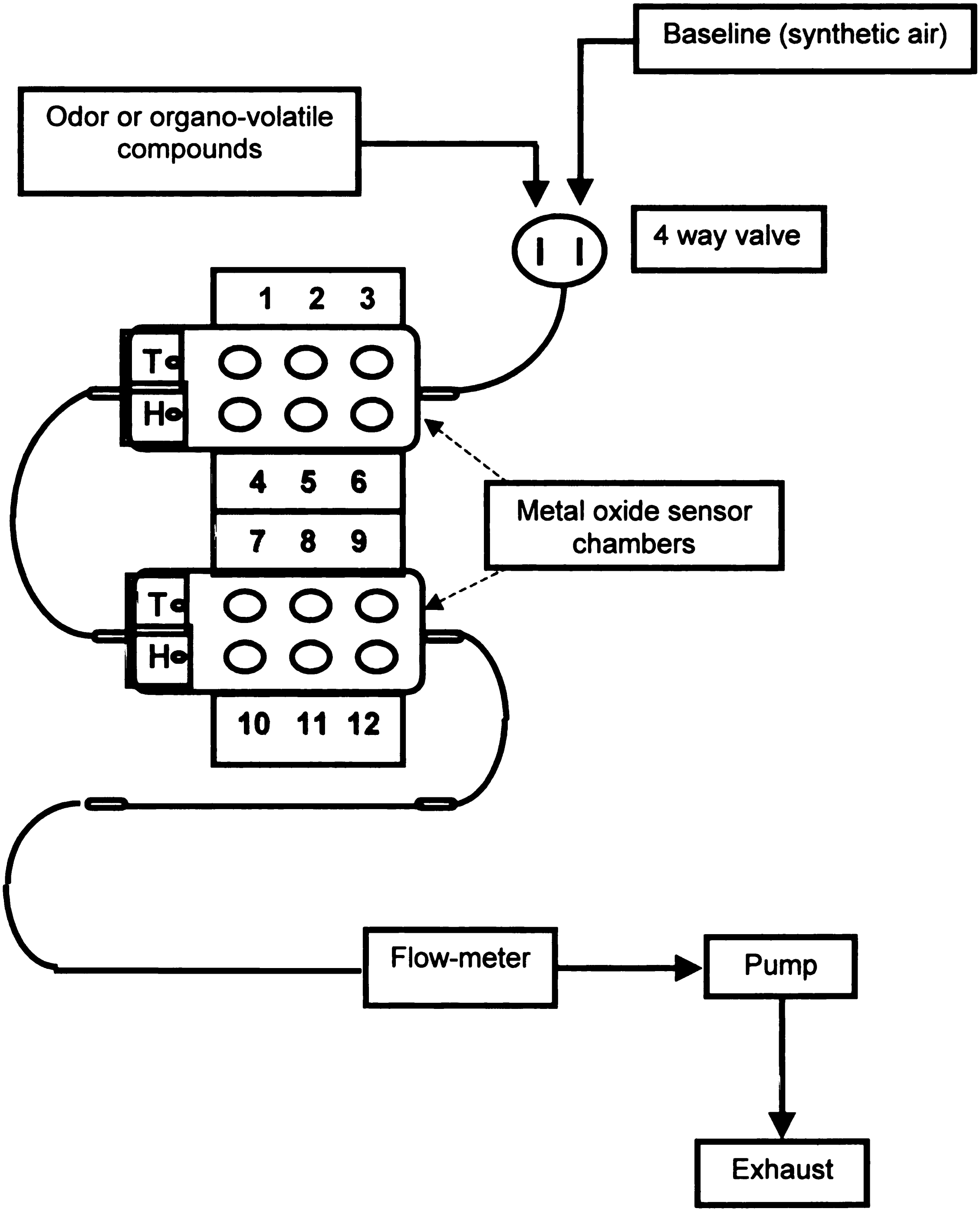

Figure 5 : Architecture of gas array sensor system (Source : Alpha M.O.S. SA, Toulouse, France)

E-nose Operation Principle

The basic operating principle of the electronic nose system involves generation of headspace over the sample being tested using heat and agitation, presentation of the headspace vapor to the sensor array system, and recording and analysis of the sensor response data using artificial intelligence or statistical data processing (Culter, 1999). Using pattern recognition software and previous human training of the E-nose, the system predicts the most likely response to the new odor fingerprint pattern, in the form of qualitative or quantitative information. The E-nose measures the aroma or odor in a way analogous to humans. However, it does not analyze or measure the components of an odor. Each chemical sensor is similar to an olfactory receptor of a human nose. The pattern recognition software used by the e-nose is analogous to the human olfactory system, which can discriminate and memorize odor responses in the cerebral cortex of the brain (Bartlett et al. 1997).

Figure6 represents the principle of the e-nose system compared to the human nose.

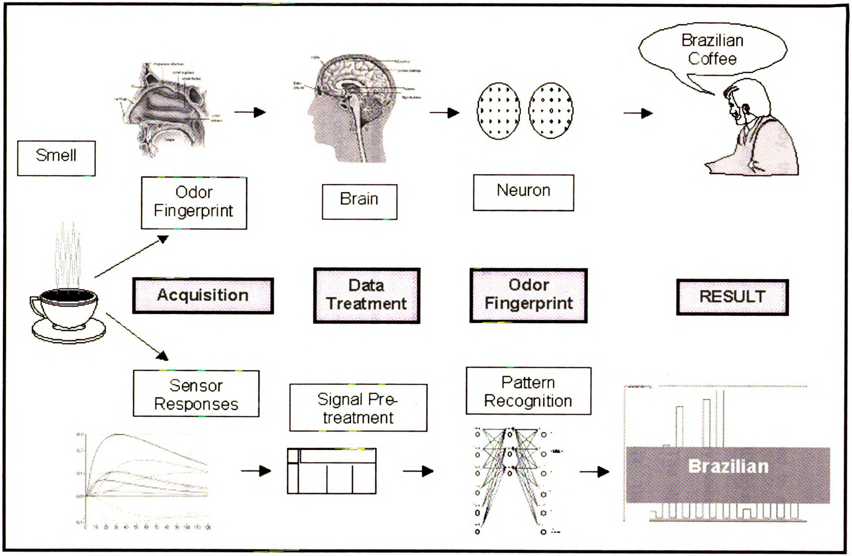

Figure 6 : Principle of Electronic Nose System (Source : Alpha M.O.S. SA, Toulouse, France)

Experimental Procedure

E-Nose procedure

In this study, the Fox 3000 E-nose system was used to analyze the olfactory profiles of eight different high-density polyethylene (HDPE) resin grades and to correlate them to the data obtained from human sensory evaluation of the drinking water samples, stored in contact with these resins. The eight different HDPE resin grades were AP, BP, CP, DX, EX, FX, GX, and HX. The first three grades were procured from a particular resin manufacturer and the remaining five were from a different manufacturer. A fixed quantity of each resin (2g) was weighed into a 10 ml glass vial and sealed. Replicates were made for each resin grade sample. The samples were loaded in the autosampler tray of the E-nose and the E-nose operation cycle was activated using the software. During the cycle, each vial was automatically transferred to the oven and agitator, to generate the headspace volatiles. The headspace volatiles were collected from the heated vial using a syringe and injected into the sensor array chamber, to generate the olfactory response profiles. Three experimental runs were conducted with variations in system parameters (Table 2).

Twelve sensor responses were obtained for the injected volatile. A pre-processing response plot was generated by the software between $\Delta R/R_o$ and time (s). $\Delta R = (R_o - R)/R_o$, where R_o is the resistance at t=0 and R is the resistance at the selected time. Between each sample volatile injection, the gas syringe was thoroughly flushed by carrier gas to avoid cross-contamination. The data obtained for the various replicates of the resin samples were analyzed by multivariate statistical treatments such as PCA and PLS to understand the degree of sample discrimination and correlation with the sensory scores of the samples. The experimental run conditions described in Table 2, which gave the highest discrimination index and a good correlation with the sensory results, were standardized for the HDPE resin grades. The response fingerprint pattern was also studied to understand the efficiency of the e-nose in discriminating various resin grades, which can be used as a valuable quality control tool.

Table 2 : System conditions used for different experimental runs

	RUN		
System Parameters	**I**	**II**	**III**
Sample replicates	4	6	6
Sample quantity (g)	2	x*	x
Incubation time (sec)	600	1200	2400
Incubation temperature (deg)	80	90	x
Agitation speed (rpm)	500	x	x
Syringe type (ml)	5	x	x
Syringe fill speed (μl/sec)	500	x	x
Syringe temperature (deg)	85	95	x
Flushing time (sec)	180	x	x
Vial type (ml)	10	x	x
Injection volume (μl)	2000	x	x
Injection speed (μl/sec)	2000	x	x
Acquisition time (sec)	120	x	x
Acquisition period (sec)	0.5	x	x
Delay (sec)	900	1080	900
Flow (ml/min)	150	x	x

x* : same value as previous run

Sensory Evaluation Procedure

The procedure for the sensory study was formulated based on guidelines obtained from Alpha MOS. An untrained consumer panel (Appendix C) was employed to detect off-flavor in drinking water samples, stored in contact with the resins.

Sample preparation

All the 8 different grades of HDPE resin pellets were soaked in ultra-pure water (in the ratio of 8:250, 8 grams of resin in 250 ml. water) for a period of one week at 40 ± 2^{o} C, in an environmental chamber. After 7 days, the stored water was vigorously agitated and filtered, to yield the 100% concentrated off-flavored water sample pertaining to each resin grade (Appendix D).

Experimental plan and design

The water samples, prepared by the above method, were presented to the untrained consumer panel for detection of off-flavor (Appendix A & B). The triangle difference test method was used, which involved determination of the odd sample in a set of three given samples. Any two given samples out of three in a triangle test are identical. This method is highly useful to determine whether an overall difference exists, which could be a result of change in ingredients, processing, packaging, or storage (Meilgaard et al. 1991). The detailed experimental layout is summarized in Figure 7.

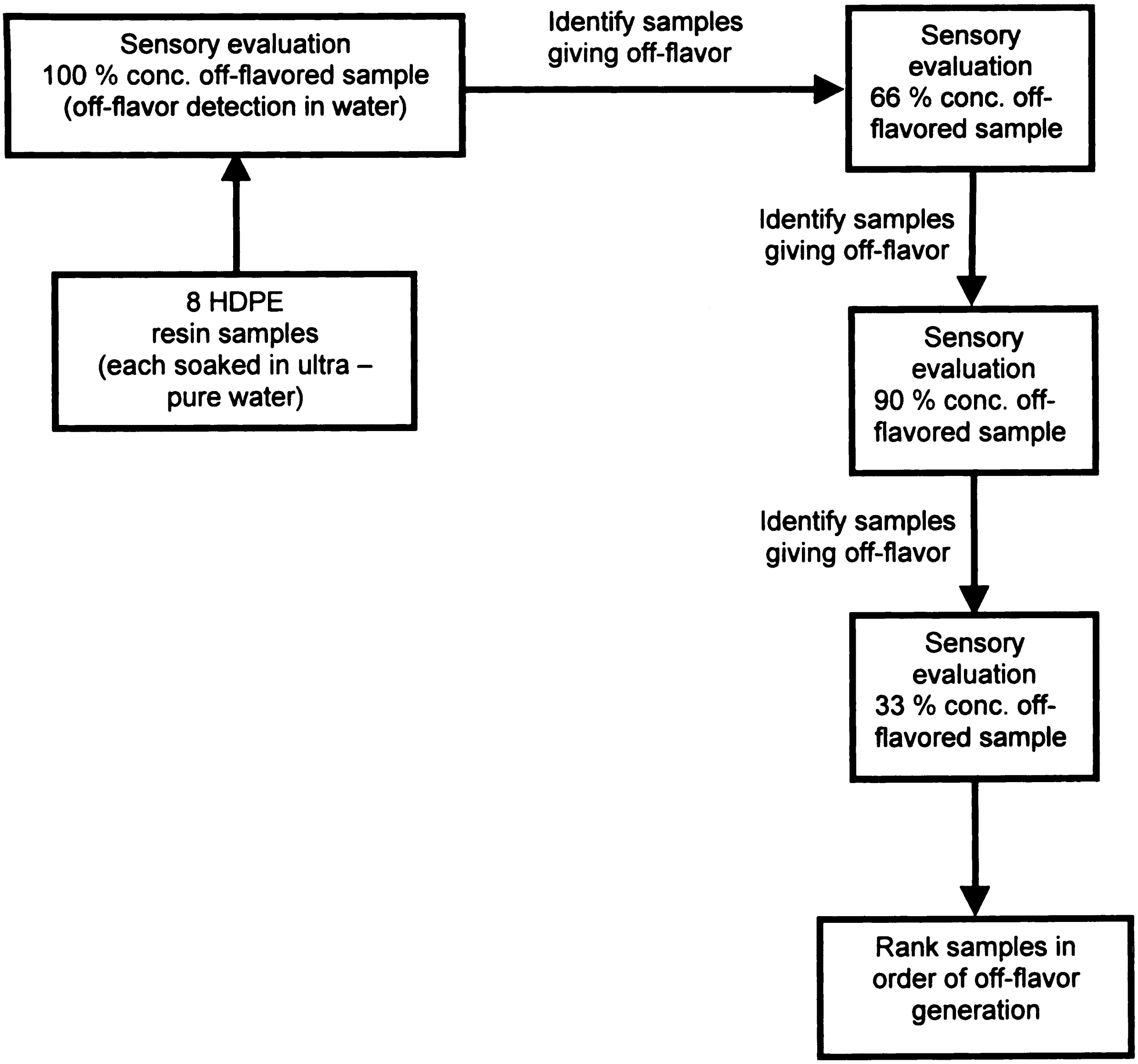

Figure 7 : Sensory evaluation experimental layout

The sample presentation was based on a randomized plan. Each subject was presented with a set of four sample sets (each being a triangle). The number of sample sets was restricted to four, in order to minimize sensory fatigue. A randomized pattern was followed for sample presentation in the triangle test, to eliminate any factor of bias during the sensory evaluation. Each sample was presented the same number of times to various human subjects (students, faculty, and staff) during each sensory experiment, which made the design quite balanced. Table 3 illustrates a section of the typical sample presentation design plan that was used.

Table 3 : Sequence of sample presentation to the consumer panel

Subject no.	I		II		III		IV	
1	WWS	7	WSS	8	SWS	2	WSW	3
2	WSS	8	WSW	5	SSW	6	WSS	3
3	SWW	7	SWW	1	WSW	3	SWS	6
4	WWS	7	SWW	4	SSW	1	SWS	3
5	WSS	2	WSW	4	SWS	8	WWS	6
6	SWS	7	SWW	2	WSW	3	SSW	5
7	WSS	1	WSW	5	WSS	4	WSS	8
8	WWS	4	WSS	8	WSW	5	SSW	3
9	SSW	3	WWS	6	WWS	5	SWW	2
10	WWS	5	WSS	8	SSW	7	SWS	3

W – Purified reference water

S – Sample (off-flavored) water (corresponding to the resin sample number in the subsequent column)

Based on the above design plan, it can be observed that the position in which a particular resin was offered to subjects was varied. For instance, Sample 8 was offered to subject 1 in the second position, subject 2 in the first position, subject 5 in the third position and subject 7 in the fourth position. Another important feature of this design was the presentation of a resin in different ways within the triangular pattern. For instance, Sample 8 was presented to subject 1 as WSS (pure water sample followed by two off-flavored samples) whereas it was presented to subject 5 as SWS (pure water sample in between two off-flavor samples). Three digit codes were used to codify the various samples so that no information could be derived by the subjects about the nature of samples or pattern of sample presentation (Appendix E).

The 100% off-flavored samples for all the eight different resin grades were presented to a consumer panel of 96 subjects, for taste evaluation. Each sample was presented 48 times according to the design plan. The samples that were found to have the most off-flavor were identified, based on the number of correct responses by the consumer panel, at a significance level of 5%. The triangle difference test method is statistically more efficient than the other sensory difference test methods e.g. paired comparison and duo-trio. The off-flavored water samples, which were differentiated by the consumer panel at 100% concentration, were further diluted to 66% concentration and presented to another untrained consumer panel, comprising of 90 human subjects. Each sample appeared 72 times in the experimental design. None of the samples were detected for off-flavor at 66%. Hence a higher concentration of 90% was prepared for the same set of off-flavored samples (detected initially at 100%) and presented to another consumer panel of 90 subjects, where each sample was presented 72 times, similar to the earlier presentation pattern. The samples having the most off-flavor were identified in a similar way.

Based on all consumer panel responses, the resins were categorized into three broad groups, depending on the severity of off-flavor generated. Sensory scores were assigned to the groups of resins, which were eventually used for correlation with the e-nose profiles. A high score was assigned to the resin producing the maximum off-flavor.

Correlation of E-nose and sensory results

Multivariate statistical techniques were used for analysis of the E-nose olfactory response data. The degree of discrimination between different resin grades was studied using principle component analysis (PCA). The correlation between the E-nose and the sensory results was determined using the partial least square technique (PLS).

Multivariate Statistical Data Analysis

Principal component analysis (PCA) was used to study the similarity or dissimilarity between the resin samples as well as to understand the relationship between the variables (E-nose sensor responses). In other words, PCA involves recognizing patterns of association in multivariate data sets. When PCA is applied to a data set, the original variables (which are the E-nose sensor responses in this case) are mathematically converted to a new set of variables, called components (Figure 8). Each component is expressed as a linear combination of the original variables.

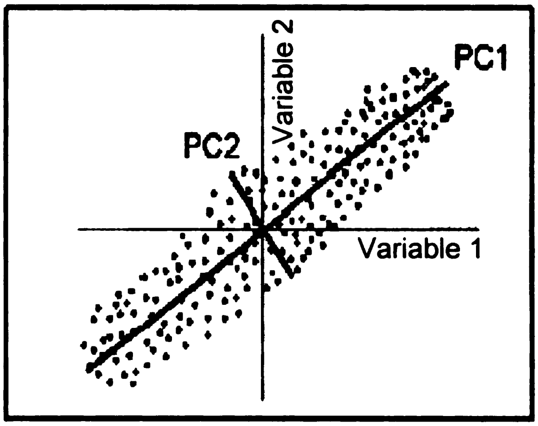

Figure 8 : Concept of PCA

The first principle component (PC1) explains the maximum amount of variation possible in one direction, for a given data set. Thus, PC1 contains the maximum amount of information. The second principle component (PC2) is orthogonal to PC1 and explains the maximum amount of remaining variation. The degree of discrimination indicates how well the sensor responses are able to distinguish between the different resin grades, based on their olfactory fingerprints. A high degree of discrimination would imply that the E-nose is capable and efficient in discriminating the various HDPE resin samples and such a procedure can be validated and standardized for similar applications.

The partial least squares (PLS) method was used to correlate the E-nose sensor responses of the different resin grades with the sensory analysis results. PLS is based on the linear regression technique, which is used to extract quantitative information. In this case, it was used to build a model that can predict the sensory panel score for any unknown HDPE resin grade, based on its E-nose sensor responses. Y is the matrix containing quantitative measurements, whereas Y' is the matrix containing the predictive values and X is the matrix built with detector (metal oxide sensor) measurements. The PLS model generates a B matrix that minimizes the distance between Y and Y' with Y' = XB. The B matrix is used to predict quantitative information (the sensory panel score) for an unknown sample. The measurement matrix is multiplied by B to obtain the prediction (Alpha MOS Fox 3000 Manual).

Chapter III

RESULTS AND DISCUSSION

Evaluation of food grade HDPE resins using the E-nose system (Standardizing E-nose run parameters)

Four replicates of eight different grades of HDPE resins were analyzed by the E-nose with Run I condition and six replicates with Run II and III conditions (Table 2). The primary idea was to establish standard run conditions, suitable to analyze such food grade HDPE resins. Principle Component Analysis (PCA) was performed on the olfactory responses of the E-nose sensors, to understand its capability to differentiate between the resin samples, based on the degree of discrimination. Twelve metal oxide sensors were used in the E-nose system. A set of twelve sensor responses was generated for each sample. PCA reduces the factor of variability between various sensor responses by a linear combination of the responses. The location of a resin in a two-dimensional PCA plot would give an idea about how different or similar it is, in comparison to other resins.

The E-nose was found to be very efficient in discriminating the resin samples, which is evident from the high discrimination indices (Run I – 93%, Run II – 88% and Run III – 88%). The high discrimination percentages in PCA profiles of the sensor responses indicated that the E-nose was successful in distinguishing between the constituent volatile components present in the various resin grades. Figure 9 (a&b) show the PCA results for Run I conditions. Figure 10 and 11 show the PCA results for Run II and III conditions, respectively.

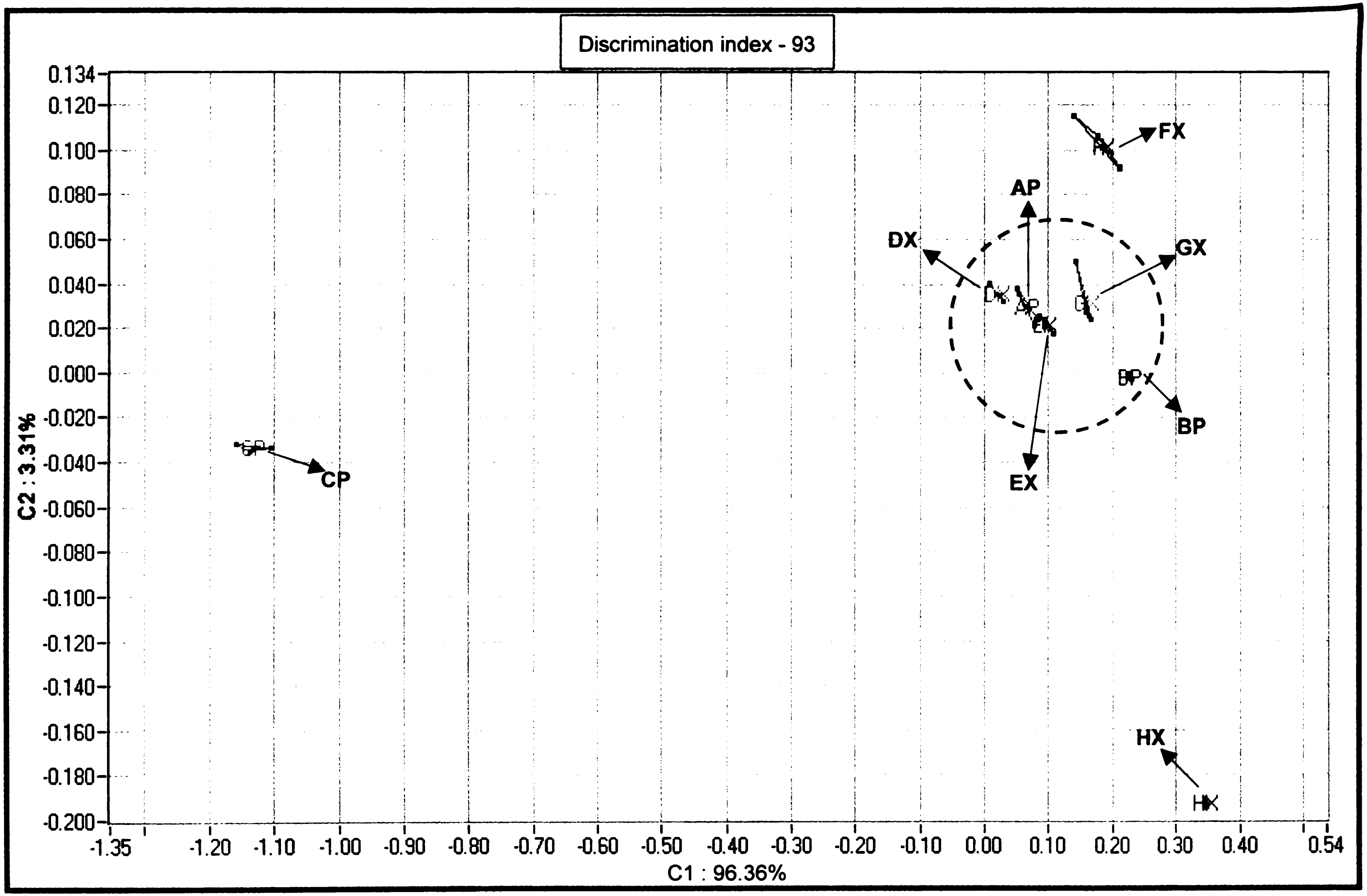

Figure 9 (a) : PCA (Run I conditions) – Discrimination among 8 resin samples by E-nose

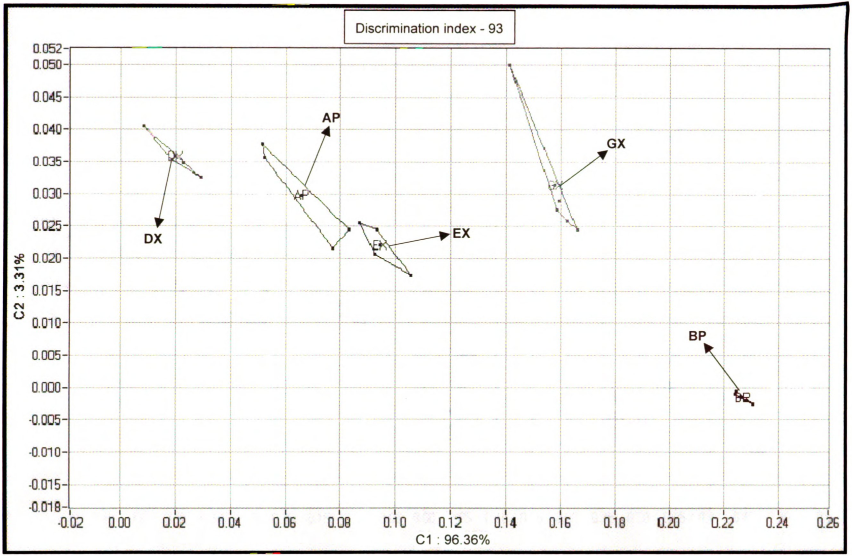

Figure 9 (b) : PCA – magnified portion (encircled in Figure 9(a)) - Good discrimination between DX, AP, EX, GX,

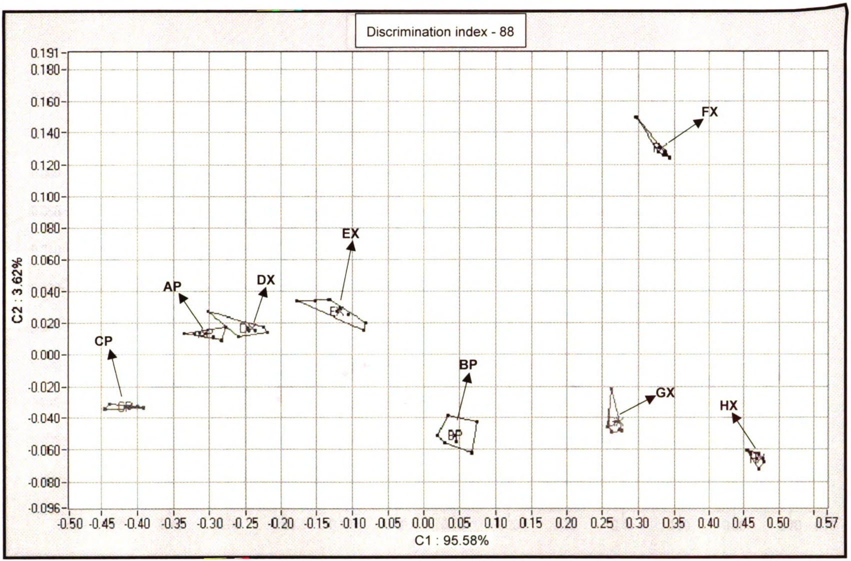

Figure 10 : PCA (Run II conditions) – Lower degree of discrimination than Run I conditions

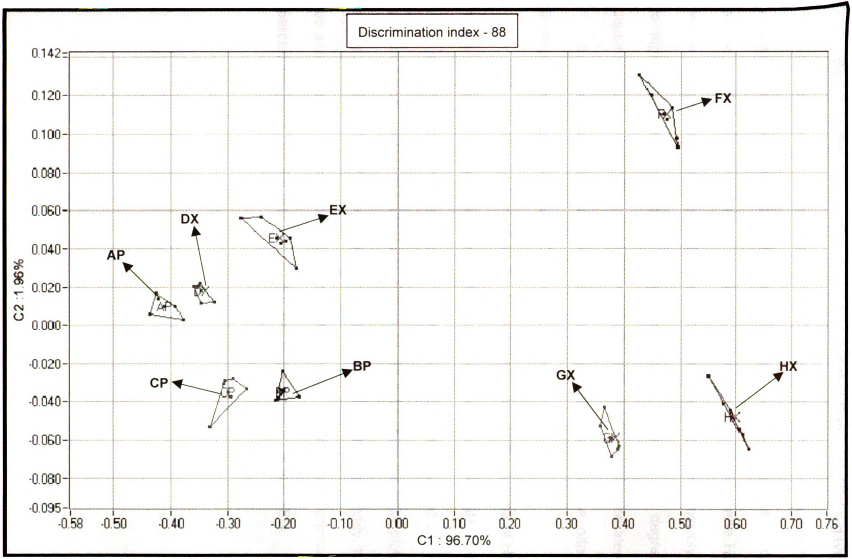

Figure 11 : PCA (Run III conditions) - Lower degree of discrimination than Run I conditions

Based on the PCA profiles, it can be seen that Run I conditions gave the highest discrimination index, i.e. 93%. The high discrimination percentage validated the experimental conditions used for Run I, which can be standardized as the most ideal set of E-nose conditions, to analyze such food grade HDPE resins. These conditions provided higher E-nose sensor responses, possibly due to higher generation of volatile compound vapors. However, the degree of discrimination was significantly high even in Runs II and III, which reiterates the fact that the E-nose is very effective in distinguishing between the olfactory fingerprints of such food grade HDPE resins.

PCA was also performed on the sensor responses of the groups of HDPE resins obtained from each source. As mentioned earlier, grades AP, BP, and CP were procured from one manufacturer whereas DX, EX, FX, GX, and HX were procured from another manufacturer. Figure 12, 13 & 14 show the PCA plots for resins AP, BP, and CP, based on Run I, II, and III conditions, respectively. It can be seen even in this case that Run I conditions gave the highest discrimination percentage (96%) for the resin set. Run II and III gave only 87% and 75%.

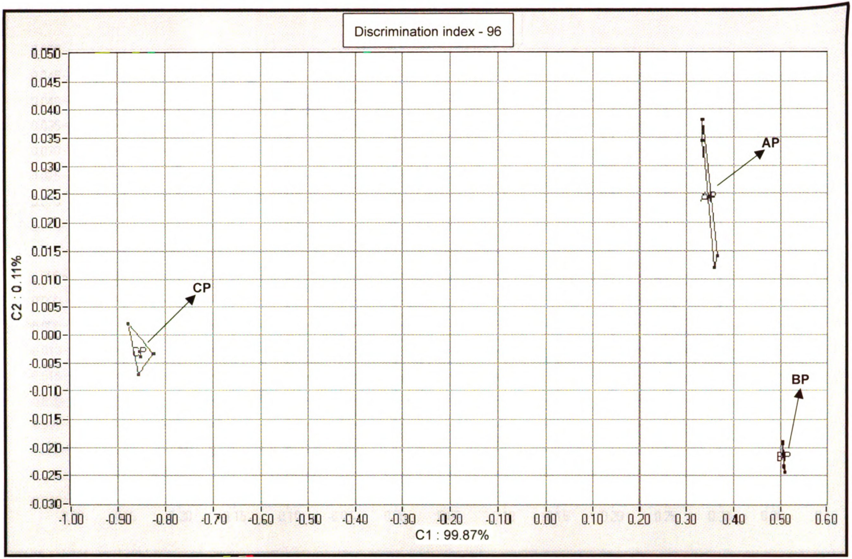

Figure 12 : PCA (Run I conditions) – High degree of discrimination between resins AP, BP, CP

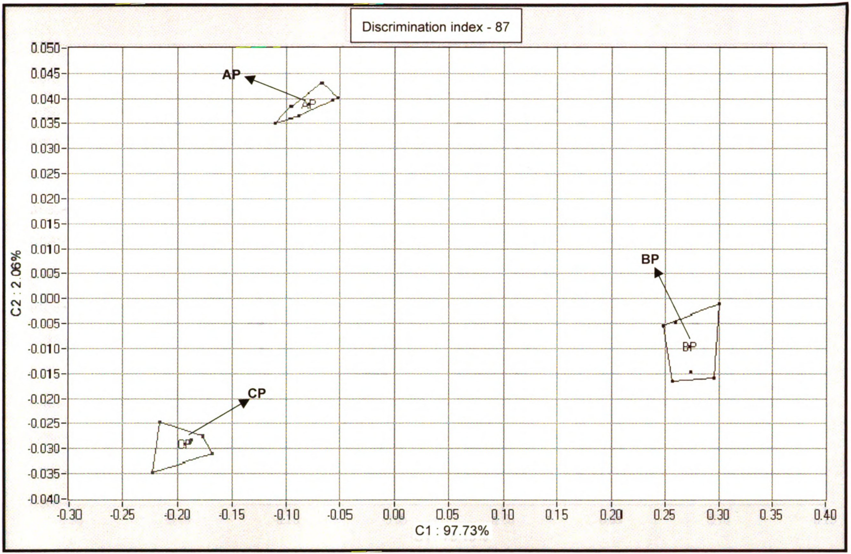

Figure 13 : PCA (Run II conditions) – resins AP, BP, CP – lower degree of discrimination than Run I conditions

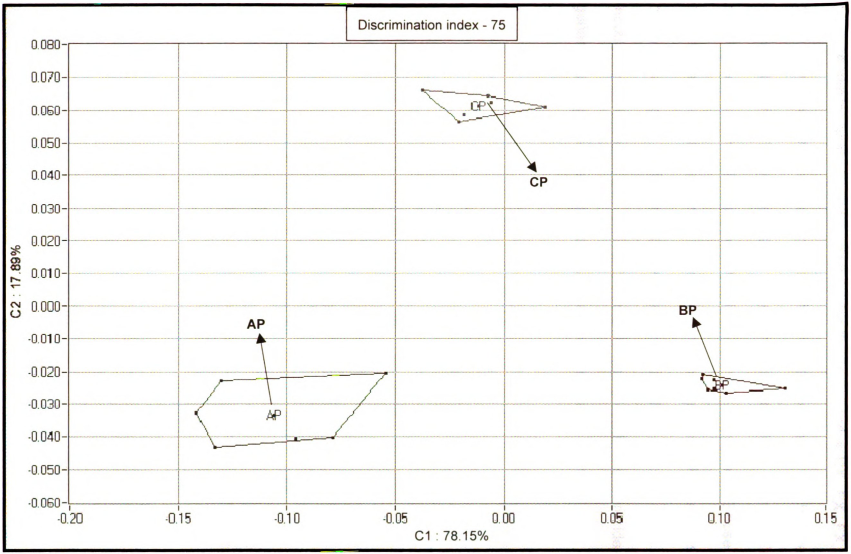

Figure 14 : PCA (Run III conditions) – resins AP, BP, CP - lower degree of discrimination than Run I conditions

A similar analysis was performed for the resin grades DX, EX, FX, GX, and HX, which were procured from a different manufacturer. It can be seen in this case that Run I gave the highest discrimination index (96%) whereas Run II and III gave 91% and 93% respectively (Figure 15, 16 & 17). Hence, E-nose Run I experimental conditions can be standardized for food grade HDPE resins, since the highest degree of discrimination was achieved in all the different cases. The incubation temperature and incubation time in Run I conditions were ideal to generate the right concentration of headspace vapors for the resins.

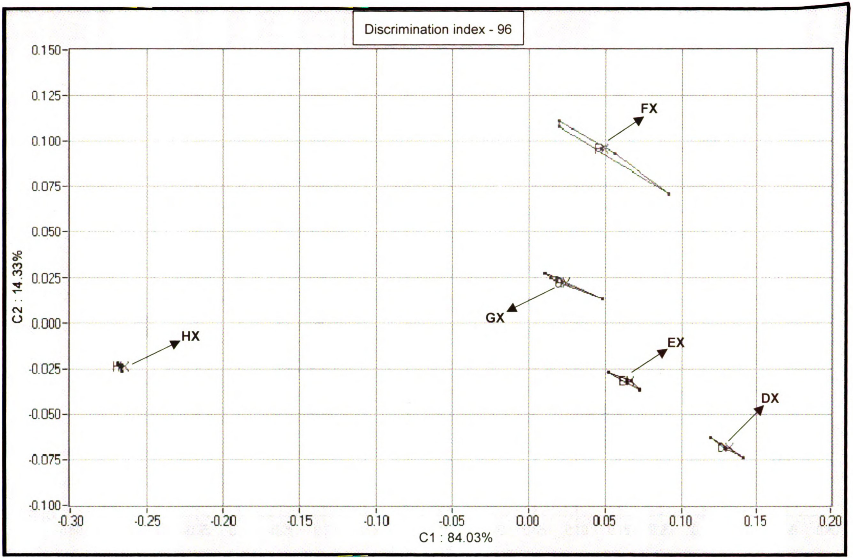

Figure 15 : PCA (Run I conditions) – high degree of discrimination between resins DX, EX, FX, GX, HX

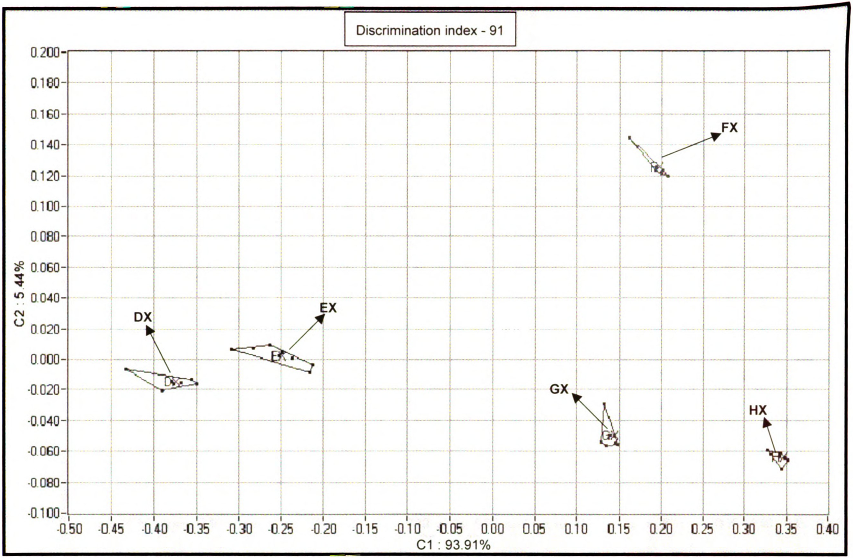

Figure 16 : PCA (Run II conditions) – resins DX, EX, FX, GX, HX – Lower degree of discrimination than Run I conditions

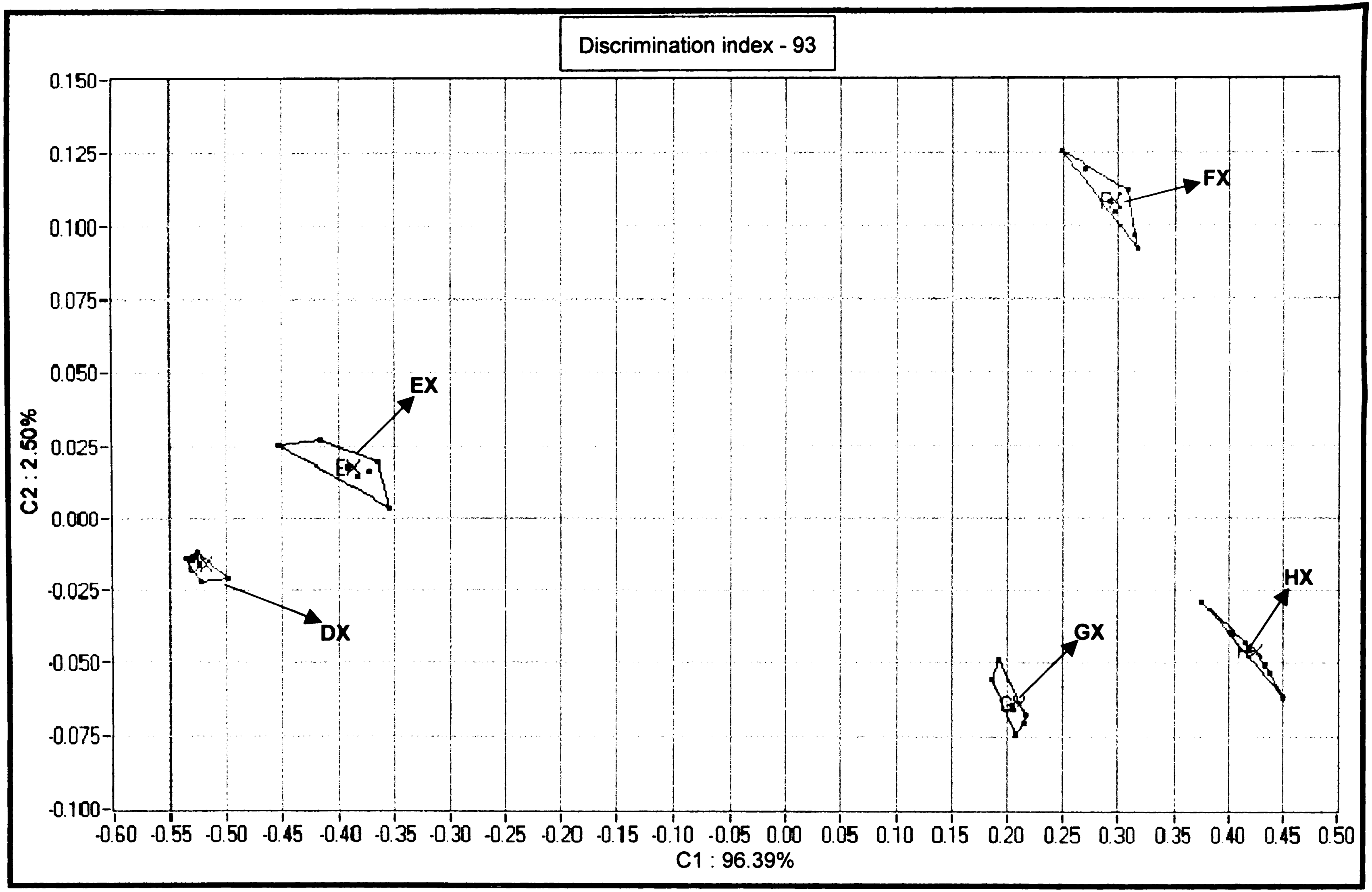

Figure 17 : PCA (Run III conditions) – resins DX, EX, FX, GX, HX – Lower discrimination than Run I conditions

E-nose sensor response comparison

A comparative study was done with the olfactory sensor profiles of Resin CP, which was understood to have a distinctively differentiating odor response, as evident from the PCA profiles. The location of Resin CP in the PCA map was found be significantly isolated from the other resin grades. This indicated the fact that the volatile composition of this grade was significantly different than the other grades. Figure 18 shows the comparison between sensor responses of Resin CP, generated by Run I and II conditions.

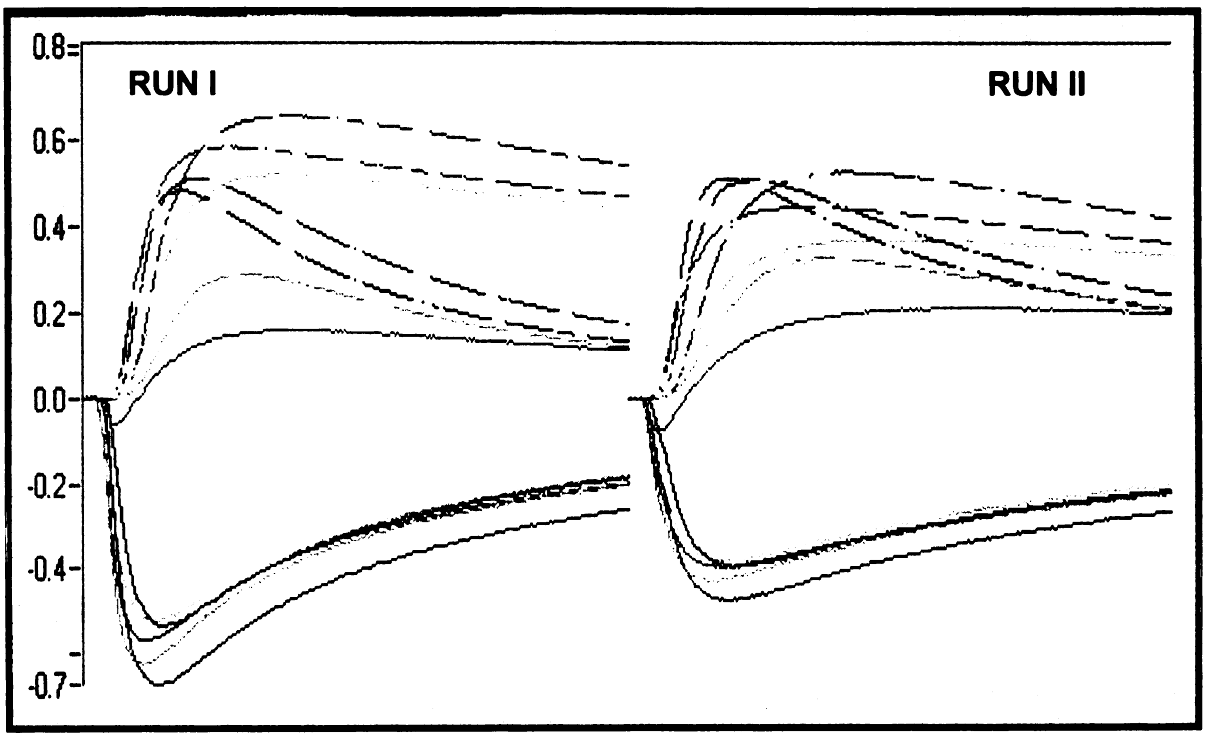

Figure 18 : Comparison of sensor responses (Resin CP) – between Run I & II
Run I – Incubation time : 600 sec; Incubation temperature : 80° C
Run II – Incubation time : 1200 sec; Incubation temperature : 90° C

The profiles shown in Figure 18 are the pre-processing plots between $\Delta R/R_o$ and time (s). $\Delta R = (R_o - R)/R_o$, where R_o is the resistance at t=0 and R is the resistance at the selected time. It can be seen that the sensor responses in Run I conditions are higher than those generated by Run II conditions. The responses can be visualized in a different format (Figure 19).

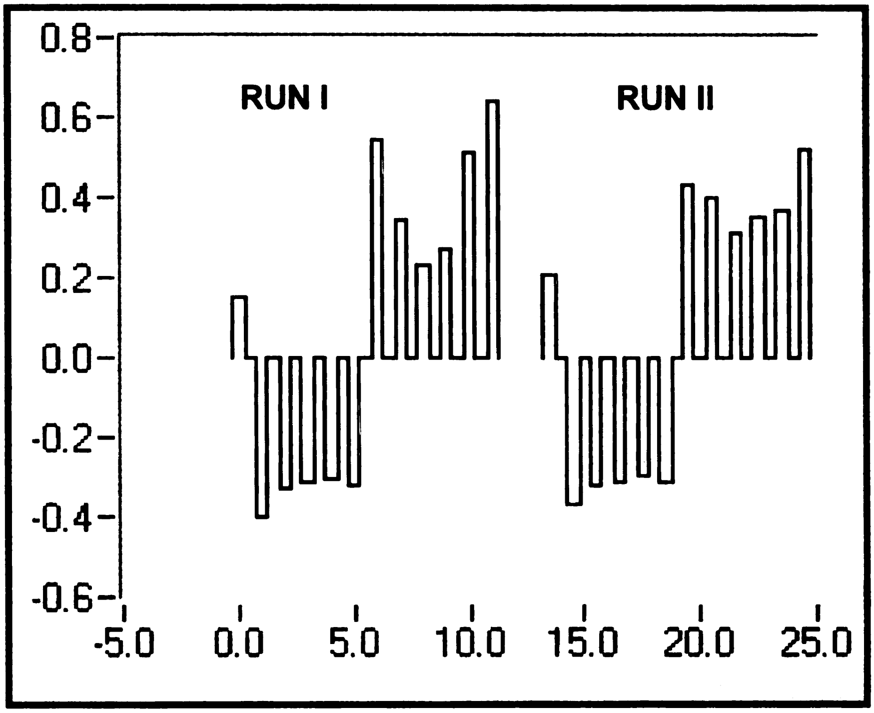

Figure 19 : Comparison of sensor responses (Resin CP) – between Run I & II
Run I – Incubation time : 600 sec; Incubation temperature : 80° C
Run II – Incubation time : 1200 sec; Incubation temperature : 90° C

A similar comparison can be made between the sensor profiles of Resin CP, generated by Run I and Run III conditions (Figure 20 & 21).

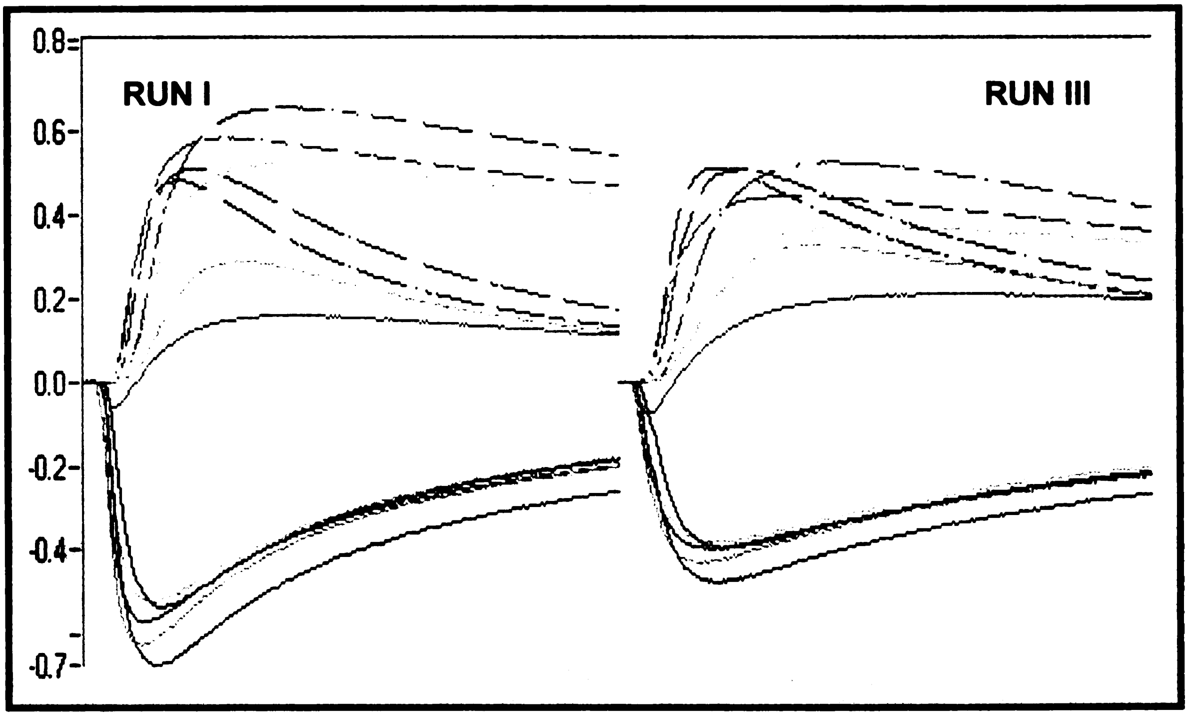

Figure 20 : Comparison of sensor responses (Resin CP) – between Run I & III
Run I – Incubation time : 600 sec; Incubation temperature : 80° C
Run III – Incubation time : 2400 sec; Incubation temperature : 90° C

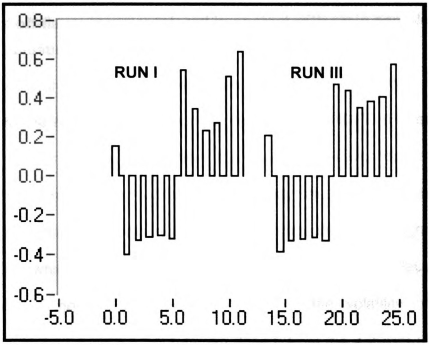

Figure 21 : Comparison of sensor responses (Resin CP) – between Run I & III
Run I – Incubation time : 600 sec; Incubation temperature : 80° C
Run III – Incubation time : 2400 sec; Incubation temperature : 90° C

It can be observed even in this case that the sensor response generated by Run I conditions was higher than the one generated by Run III conditions. Thus it can be seen that the sensor response generated using Run I conditions was the highest of the three. This reiterates the validation of the Run I experimental conditions, which are ideal for analysis of food grade HDPE resin grades. The higher sensor response was attributed to a higher concentration of volatiles generated in the headspace, which eventually led to a higher degree of discrimination between the resin grades, as evident from the PCA profiles. This also indicates the reliability and effectiveness of the E-nose system in differentiating between the resin samples, based on their volatile compositions.

Analysis of off-flavor in water (stored in contact with resin samples)

Sensory Evaluation

Odor-threshold, molecular weight, and polarity are three main factors that contribute to the release of off-flavor compounds from HDPE (Ho et al. 1994). The lower the odor threshold, the easier it is to detect off-flavor for the consumer. Compounds having very low odor thresholds may cause off-flavor problems in water, even in trace amounts. Typically, the compounds that migrate into the food product, which is drinking water in this case, have low molecular weight. The lower the molecular weight, the higher is the volatility of the odor compounds. Hence such compounds can desorb from the polymer matrix to the gas phase at a faster rate than the other high volatile compounds, which may further migrate into the water sample. Polar compounds have a higher tendency to escape out of a non-polar matrix. Hence low molecular weight polar volatiles can easily migrate into water and cause off-flavor problems (Maneesin, 2001). The volatiles generated in the HDPE resin sample headspace, by the E-nose, can be attributed to release of such lower molecular weight polar compounds from the polymer matrix.

An organoleptic study was conducted on drinking water samples that were stored in contact with the eight different grades of HDPE resins at 40 $\pm$ 2° C for 1 week. The idea was to rank the resin grades based on the degree of off-flavor generated. The triangle difference test method was followed, using an untrained consumer panel.

As a part of the sensory evaluation procedure, water samples were initially presented to the consumer panel at a 100% concentration level. Five out of eight samples (which were stored in contact with the respective resin grades) were found to having undesirable off-flavor. The off-flavored water samples were further diluted to 66% concentration and presented to another untrained consumer panel. None of the samples were detected for off-flavor at 66%. Hence a higher concentration of 90% was prepared for these five off-flavored samples (detected initially at 100%) and presented to another consumer panel. Resin grade CP was the only resin detected for off-flavor at the 90% concentration level. Table 4 shows the consumer panel response in detecting off-flavor at different concentrations of water.

Table 4: Consumer panel response for off-flavor in different water concentrations at significance level of 5% (probability, $p \leq 0.05$)

Resin	**100% conc.**		**66% conc.**		**90% conc.**	
grades	**Correct**	**Incorrect**	**Correct**	**Incorrect**	**Correct**	**Incorrect**
AP	22	26	26	46	28	44
BP	16	32	-	-	-	-
CP	22	26	24	48	36	36
DX	25	23	22	50	27	45
EX	18	30	-	-	-	-
FX	30	18	24	48	28	44
GX	27	21	19	53	27	45
HX	10	38	-	-	-	
	Number of subjects = 96		Number of subjects = 90		Number of subjects = 90	
	Each sample presented 48 times in this plan		Each sample presented 72 times in this plan		Each sample presented 72 times in this plan	

As seen in Table 4, resins AP, CP, DX, FX, and GX were detected for off-flavor at 100% concentration (shaded), and were further presented at 66%

concentration to a later panel. No off-flavor was detected for any of the samples. Off-flavor was detected for the water stored in contact with resin grade CP at 90% concentration. The minimum required number of correct responses for number of respondents, n = 48, is 22 at the 5% significance level. Similarly, the minimum required number of correct responses for number of respondents, n = 72, is 32 at the 5% significance level (Meilgaard et al. 1991, Table T7).

Based on the consumer panel responses, the resins were categorized into 3 broad groups, depending on the severity of off-flavor generated. Sensory scores were assigned to the groups of resins, which were eventually used for correlation with the e-nose profiles. A high score was assigned to the resin producing the maximum off-flavor. Table 5 shows the sensory scores assigned to different groups of resins.

Table 5 : Sensory scores (resins categorized into 3 groups, based on the sensory panel response) – A high score was assigned to the resin that generated the most off-flavor in water

Scores		
1	**2**	**3**
BP	AP	CP
EX	GX	
HX	DX	
	FX	

Correlation of E-nose and sensory responses

The olfactory data generated by the E-nose for all the resin samples were correlated with the sensory panel results using the Partial Least Squares (PLS) linear regression model. Figure 22 (a&b) shows the correlation between the expected (based on actual consumer panel response) and predicted values (based on the e-nose sensor responses), for the resin olfactory data obtained using Run I conditions. Any scoring scale can be used for the sensory data, provided the difference between the assigned scores remains the same. This is evident from Figure 22 (a) where scores 1, 2 & 3 were assigned and Fig 22 (b) where 1, 3 & 5 were assigned. The correlation percentage did not change in both cases.

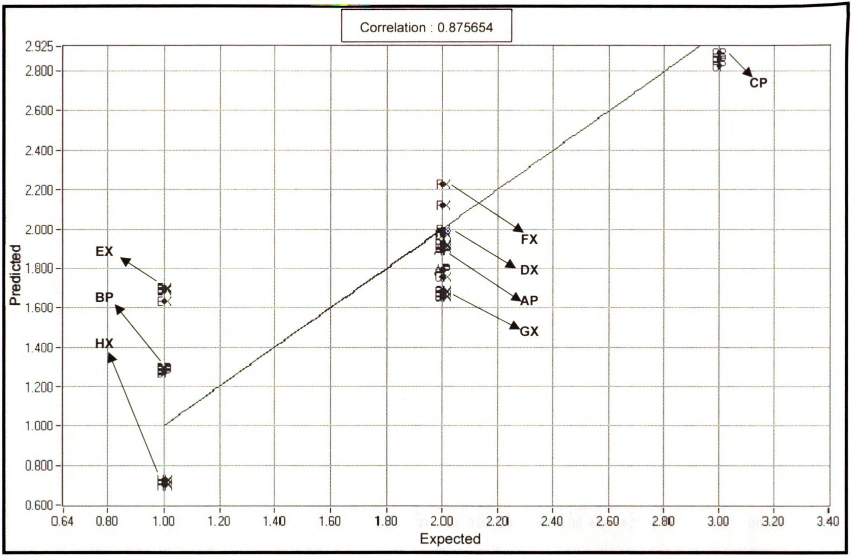

Figure 22 (a) : Correlation between expected and predicted values for Run I conditions (assigned scores – 1,2,3)

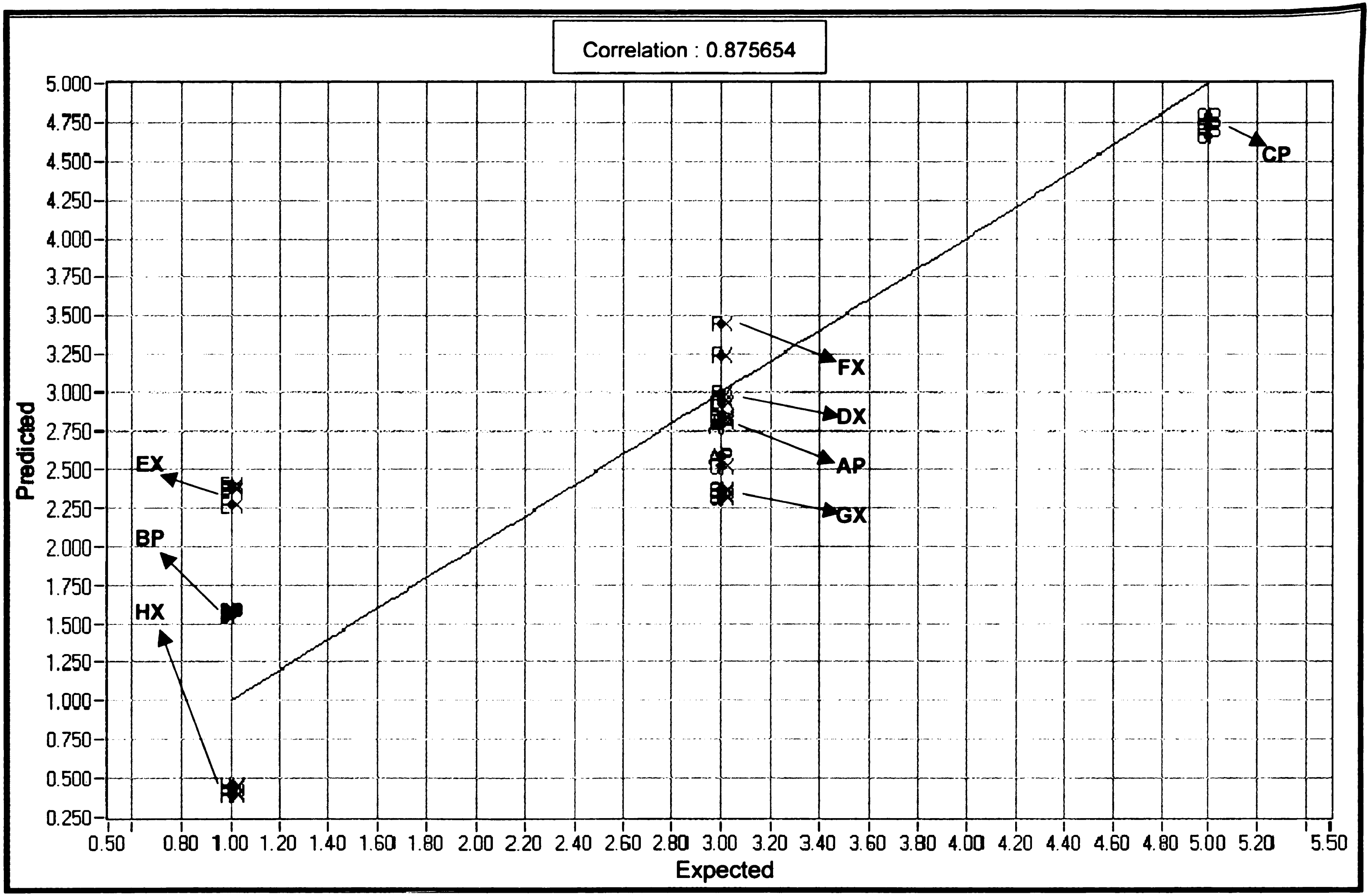

Figure 22 (b) : Correlation between expected and predicted values for Run I conditions (assigned scores – 1,3,5)

As is evident from Figure 22 (a&b), a good correlation percentage (87.5%) was obtained between the expected and predicted values. The predicted values are generated by the E-nose, based on the sensor responses of the different resin grades. If an unknown HDPE resin is analyzed by E-nose, a predicted value can be obtained for it based on its sensor response. Based on the linear correlation model, an expected sensory score can be estimated, which would be a true indication of an actual sensory score based on an organoleptic response from a consumer panel. The need for continual sensory evaluation by a real time consumer panel can be eliminated. The correlation models obtained for Run II and III conditions are shown in Figure 23 and 24, respectively.

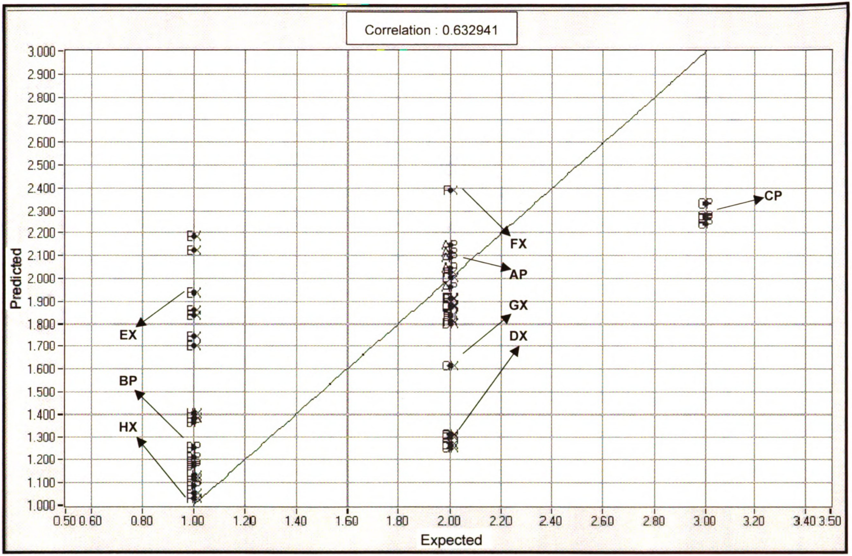

Figure 23 : Correlation between expected and predicted values for Run II conditions

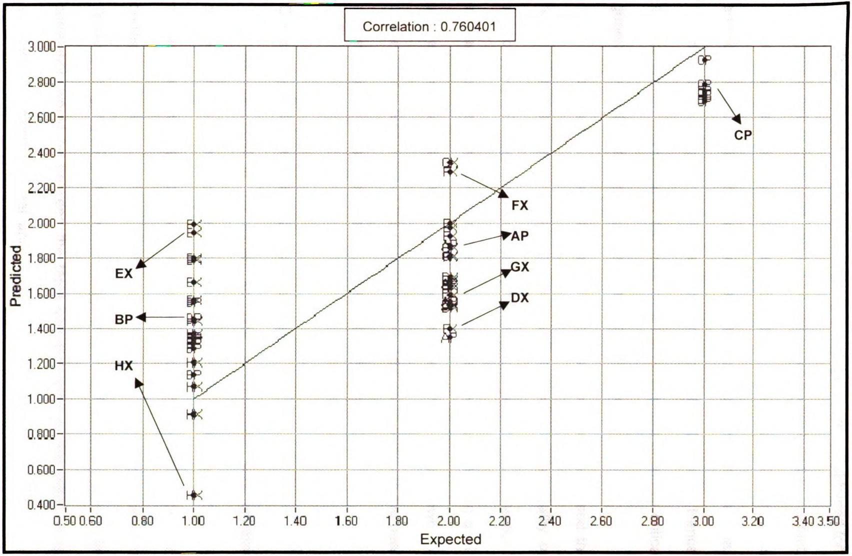

Figure 24 : Correlation between expected and predicted values for Run III conditions

It can be seen that high correlation percentages were not obtained for Run conditions II and III (63% and 76%). This can again be attributed to the fact that higher sensor responses were not obtained for Run II and III conditions. In addition, a high correlation percentage for Run I conditions validates that the Run I conditions are the most ideal to analyze food grade HDPE resins. Hence the standardization and usage of the most ideal run parameters becomes critical for generating reliable and reproducible data from the E-nose.

A correlation between the actual human sensory responses and the E-nose sensor responses becomes very useful in predicting the quality of an unknown HDPE resin. A successful prediction can also be made about how similar or different the unknown resin is in comparison to known resin qualities, as the E-nose would assign an expected sensory score to the unknown, based on the sensor responses of the unknown resin. This could eliminate the need for a formal human sensory evaluation of the unknown sample.

E-nose analysis of off-flavored water samples

As discussed in the earlier sections, a correlation was established between the E-nose sensor responses of the HDPE resins and the sensory characteristics of the water samples, stored in contact with the resins. Such a correlation would be useful in predicting the quality of the resins, in terms of its likelihood of generating off-flavor in the water sample. However, a more intimate correlation would be between the taste characteristics of the water samples, evaluated by sensory panel and E-nose sensor responses of the same off-flavored water samples. An effort was made to analyze the off-flavored water samples (stored in contact with the resins), using the E-nose. The idea was to understand whether the E-nose was capable of discriminating between the water samples and effectively correlating the sensor responses with the human sensory scores. Two different experimental run conditions were tried in the E-nose, involving variations in incubation time and temperature. It was found that E-nose sensors were not capable of discriminating between the different water samples in both cases. This is evident from negative discrimination percentage obtained in the PCA profile (Appendix F). It was also difficult to establish standard experimental run conditions, suitable for analyzing water samples.

CHAPTER IV

CONCLUSIONS

AND

RECOMMENDATIONS FOR FUTURE WORK

In this study a standard method for analyzing the quality of food grade HDPE resins was developed, using the E-nose. The method is capable of predicting the quality of an unknown food grade HDPE resin sample, in terms of its possibility of producing an off-flavor in drinking water, as a result of migration of low molecular weight compounds from the polymer. This is evident from the high correlation percentage in the PLS model, which indicates a good correlation between the E-nose sensor responses and human sensory scores for the resin samples. Such an experimental method may completely substitute for the sensory evaluation techniques, which are currently being used for this application, with a simpler qualitative and quantitative data analysis, offering better reliability and reproducibility of results.

A much better correlation between the sensor responses and the human sensory scores could be obtained if the water samples were discriminated more distinctly by the human sensory panel. This would have facilitated a better ranking of the resins based on the degree of off-flavor generated in the water samples, unlike categorizing into three broad groups, as done in this case. One of the main reasons for not being able to achieve a clear sensory ranking, with a distinct sensory score attributed to each resin, is the use of untrained consumer panel. Determining off-taste in water sample is often a very difficult task and needs good understanding and sense of taste perception, which can be developed only among trained panelists. Thus use of a trained sensory panel would certainly be a positive step ahead in this area of research.

The work also validated the sensitivity and efficiency of the E-nose sensors for analyzing HDPE resin samples. This is evident from the high discrimination percentage in the PCA profiles. The ideal experimental conditions required to analyze food grade HDPE resins have also been validated and standardized. However the E-nose sensors were not found to be capable of discriminating between off-flavored water samples. A more sensitive set of E-nose sensors is recommended for this application, which might even require training of the E-nose to some extent. A good discrimination between the water samples can prove highly useful in achieving more meaningful correlation between the E-nose olfactory responses and human sensory data, which is a potential area of future research.

The E-nose is capable of performing a variety of multivariate statistical techniques, which can be used for numerous packaging and food applications. The E-nose can certainly be considered as a powerful and effective quality evaluation and control tool for diverse packaging applications.

APPENDICES

APPENDIX A

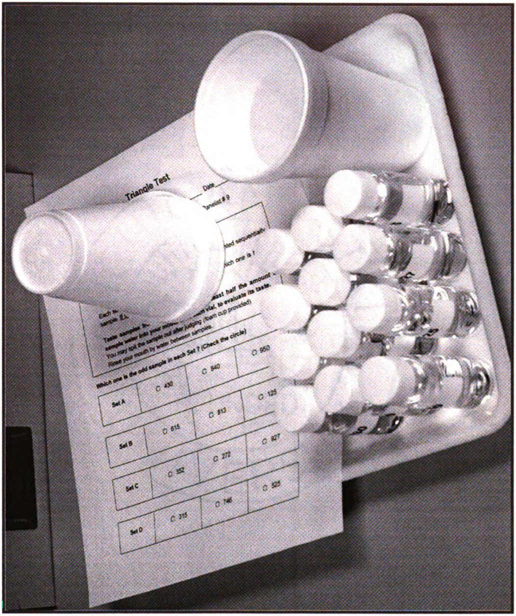

Figure 25 : Tray with water samples provided to consumer panel (Triangle Test)

APPENDIX B

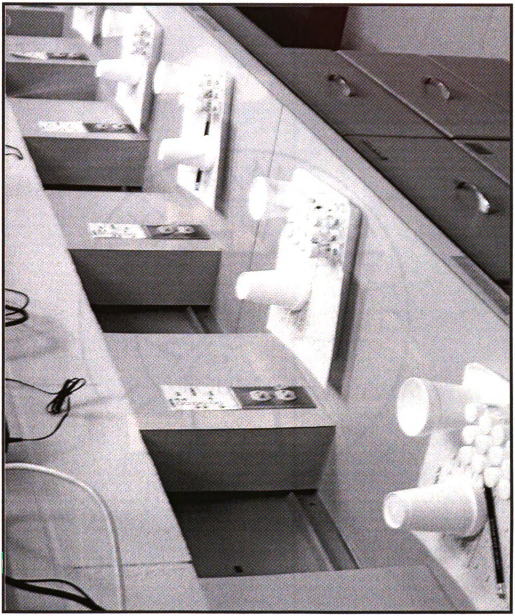

Figure 26 : Kitchen area (sample trays are presented through the booth windows)

APPENDIX C

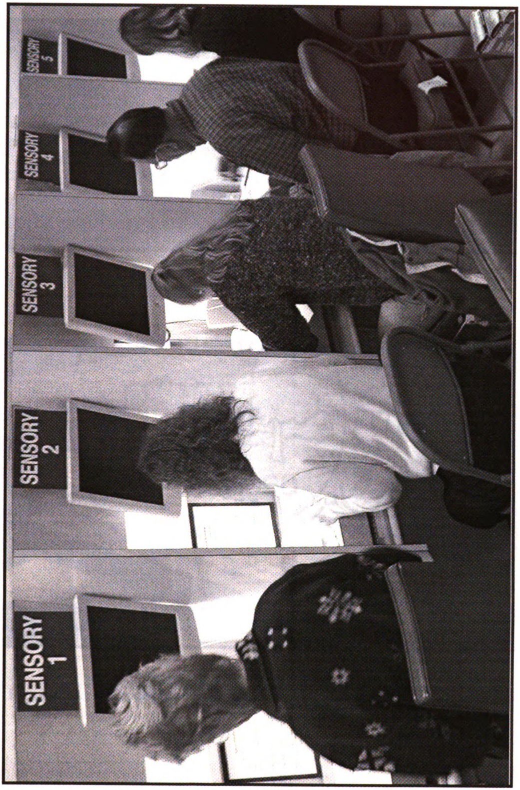

Figure 27 : Sensory evaluation in progress (consumer panel)

APPENDIX D

Figure 28 : Vials containing water samples, used for sensory evaluation

APPENDIX E

Triangle Test

Name : ________________ Gender :____ Age : _____ Date_________

Sample : **Water (stored in contact with plastic)** Panelist # 5

INSTRUCTIONS

- Four independent sets (A, B, C, D) of samples are presented sequentially.
- Each set has 3 samples; 2 are identical. Determine which one is the odd sample. <u>If no difference is apparent, you must guess</u>.
- **Taste samples from left to right.**
- **Take at least half amount of the water into your mouth from each vial, to get a feel of its taste.**
  You may spit the sample out after judging (foam cup provided)
  Rinse your mouth by water between samples.

Which one is the odd sample in each Set ? (Check the circle)

Set A	○ 950	○ 150	○ 581
Set B	○ 615	○ 407	○ 176
Set C	○ 977	○ 813	○ 764
Set D	○ 352	○ 525	○ 718

Figure 29 : Questionnaire for sensory evaluation (Triangle test)

APPENDIX F

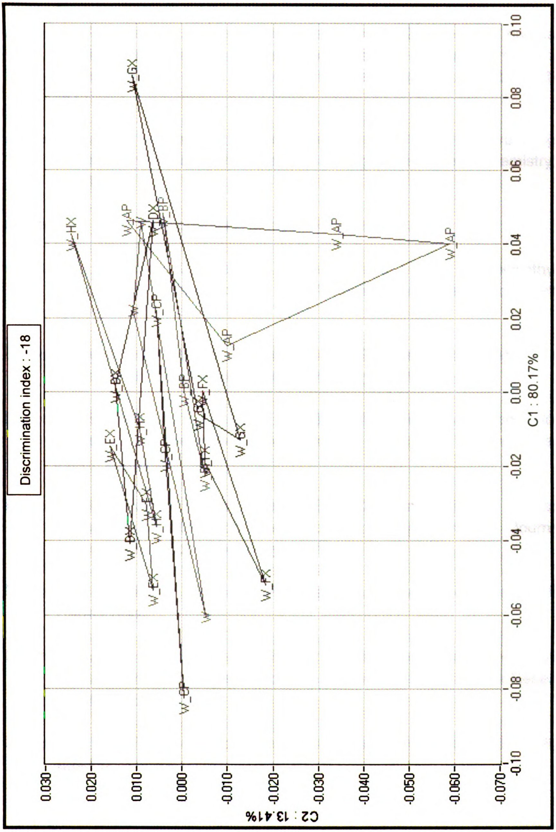

Figure 30 : PCA – No discrimination among off-flavored water samples and reference water (negative index)

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