GC-MS AND ELECTRONIC NOSE ANALYSIS ON OFF-FLAVOR COMPONENTS IN HDPE CONTIANERS AND CORRELATION WITH SENSORY EVALUATION

BY

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ABSTRACT

GC-MS AND ELECTRONIC NOSE ANALYSIS OF OFF-FLAVOR COMPONENTS IN HDPE CONTAINERS AND CORRELATION WITH SENSORY EVALUATION

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Evaluation of off-odor from one gallon HDPE water containers was carried out using an electronic nose system (e-nose), GC-MS and sensory evaluation. In order to determine the effect of antioxidants and processing conditions on the release of volatile compounds from HDPE containers, container samples were fabricated using two antioxidants; α-Tocopherol and Irganox 1010 at two processing temperature conditions; normal (174°C) and abusive (204°C).

The e-nose system with Principal Components Analysis was capable of discriminating between volatiles released from the HDPE container samples produced using different antioxidants. This was in good agreement with GC-MS analysis. The e-nose system also demonstrated its potential to differentiate between volatiles released from the HDPE containers produced at 174°C and 204°C.

HDPE containers were filled with highly purified water and stored for six months. The water samples were then subjected to e-nose, GC-MS, and sensory analysis every three months. GC-MS analysis showed that higher nonanal levels were found in water packaged in the HDPE containers after

storage indicating migration of some volatile compounds from HDPE containers into water. The water packaged in the HDPE containers also had higher unacceptable scores in comparison to water packaged in the glass container (reference) as revealed by sensory evaluation. After three months storage, Irganox 1010 samples produced at 204°C had the highest nonanal level, as well as the highest unacceptable score by the panelists. However, correlation between sensory evaluation and the e-nose system was not conclusive due to the low e-nose sensor responses from the water samples.

To the memory of… Dr. Jack R. Giacin…

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INTRODUCTION

Polymeric packaging is commonly used in the food industry because it has many advantages, such as: durability, flexibility, lightweight and low cost. However, plastic packaging is not inert, and physical and chemical interaction may occur with food products. The transfer of low molecular weight organic compounds from, as well as their uptake by, polymers has been reported extensively in the literature (Passey, 1983; Risch, 1988; Koszinowski and Piringer, 1986; Kim-Kang, 1990; Culter, 1992). Volatile compounds in packaging materials arise most commonly from solvents, coatings, inks and adhesives. Further, they can also originate from polymer related sources, such as low molecular weight fractions, breakdown products, and impurities from production processes (Gilbert, 1978; Crompton, 1979; Shepherd, 1982; Kim-Kang, 1990). Migration or transfer of low molecular weight components from a polymer, i.e. packaging material, to a contained food product, can result in a change in flavor and affect the perceived quality of the product (Peled and Mannheim, 1977; Koszinowski and Piringer, 1986; Bravo et al., 1992; Leong et al., 1992; Linssen, et al., 1993; Ho et al., 1994; Yam et al., 1996; Van Leeuwen et al., 1998). Today, consumers are increasingly concerned about the safety and quality of food products. Thus, establishing appropriate quality control procedures is mandatory to assure quality products.

It is often difficult to trace the source of off-odors and off-flavors in food. In general, compounds responsible for off-flavors and off-odors have very low detection thresholds, often lower than the detection limits of the analytical instruments available. For instance, migration products may occur at levels of parts per billion (ppb; weight/weight) or lower (Risch, 1988; Koszinowski and Piringer, 1986; Thompson et al., 1994). Gas chromatography-mass spectroscopy (GC-MS) techniques can separate complex vapor mixtures into the respective individual compounds with high sensitivity. However, the results are not in a form that can be directly related to data obtained from sensory analysis. Sensory panels provide results, which can be related to human perception of the product. However, all individuals are not equally sensitive to taste and odor.

Electronic olfactory sensing systems or electronic nose systems are instruments designed to mimic the human olfactory sensory system and can analyze an aroma profile without separating it into its individual components. This approach has proven successful for analysis of a wide range of products, including foods, drinks, flavorings and perfumes (Persaud and Pelosi, 1985; Hodgins and Simmons, 1995; Tan et al., 1995; Pitt, 1996). Undoubtedly, these systems can be used in packaging applications such as detection of taints in plastic food containers, spotting non-set glues on food wrappers or identifying problems with carton and paperboard packaging (Pitt, 1996). Potential applications of electronic nose systems to the packaging industry are summarized below;

- Detection of residual solvents released from printing inks, coatings and adhesives for quality control of incoming materials such as flexible packaging, coupons and labels, and sealant layer.

- Detection of residual organic materials from returnable and refillable packaging prior to filling.
- Detection of organic volatiles formed by the oxidation of a polymer during fabrication, e.g. high density polyethylene (HDPE) blow-molded bottles.
- A qualitative tool for monitoring loss of flavor, fragrance and organic vapor from a product/package system.

High density polyethylene (HDPE) is one of the most versatile polymers used in packaging (Jenkins and Harrington, 1991) and can be readily converted to film, sheet and containers. It is the most widely used of the three basic types of polyethylene resins in the United States. In the year 2000, approximately 7.1 million tons of HDPE resins were supplied in the US and Canada (Modern Plastics, February 2001). Blow molding of food containers is one of the major uses for HDPE resins.

Degradation of the HDPE polymer may yield low molecular weight moieties that can transfer to a contained food product resulting in an off-odor. For example, Ho et al. (1994) identified the presence of off-odor compounds from HDPE bottles using a purge and trap GC-MS procedure. The authors identified 47 volatile compounds, ranging from C_6-C_{18} in chain length, and functionality that included: n-alkanes, 1-alkenes, aldehydes, ketones, phenolics, olefins and paraffins. Among them, aldehydes and ketones were predominant, due to their low odor threshold.

The transfer of low volatile compounds often occurs at the packaging surface. Thus, surface interaction with a product is critical to the long-term performance of any packaging polymer. Advanced development in surface analysis techniques, which can provide information on the surface and interfacial chemistry of packaging materials is useful in product development, quality control, and failure analysis. Successful examples of Fourier Transform-Infrared Spectrophotometry (FT-IR) and Electron Spectroscopy for Chemical Analysis (ESCA) for surface monitoring in packaging applications have been reported (Briggs, 1996, Fay, 1993, West, 1996; Swift and West, 1998).

Van Leeuwen et al. (1998) also investigated the oxidation level on surfaces of LDPE cast films after production and storage using FT-IR and ESCA measurement. The results showed a rapid increase in oxygen concentration on the surface after 12 weeks of storage for the LDPE sample processed without antioxidant. The oxidation level was fairly constant for the LDPE sample which contained vitamin E as antioxidant.

In this study, an electronic nose system was evaluated as a tool for use in quality assurance in a packaging application. To achieve this goal, the sensitivity and the detection threshold of the instrument was investigated. Monitoring of off-odor compounds from the packaging material was carried out on HDPE blow-molded bottles, using the electronic nose system, GC-MS analysis and sensory evaluation. In addition, surface analysis was conducted using FT-IR and ESCA techniques, in order to provide more information on the surface characteristics of the bottles. Finally, the relationship between transferable volatile organic compounds and quality change in drinking water was determined, and correlated to the electronic nose system responses. In these studies, the Fox 3000 electronic nose system [Alpha M.O.S. America (Hillsborough, NJ)] was employed.

The specific objectives of the study include:

1. To determine the sensitivity and selectivity of the metal oxide sensors used in the Fox 3000, electronic nose system.
2. To identify and quantify selected volatile off-odor compounds released from HDPE containers using GC-MS analysis.
3. To determine the extent of off-odor compounds released from one gallon HDPE water containers as a function of processing variables including temperature and the nature of the antioxidant, using both sensory evaluation and instrumental analysis.
4. To calculate oxidation indices of the HDPE container surface, as a function of processing parameters, using Fourier Transform-Infrared (FT-IR) spectrophotometry and Electron Spectroscopy for Chemical Analysis (ESCA).
5. To develop a correlation between the results obtained from the electronic nose system, GC-MS analysis and sensory evaluation.

The goal of this study was to evaluate the e-nose system as a quality control tool for use in packaging applications and to develop a correlation between the results obtained from the e-nose system, GC-MS analysis and sensory evaluation. The e-nose system has an analytical capability, which could be a benefit to quality control, and quality assurance laboratories. E-nose systems continue to evolve with regards to sensor technology and software development for data interpretation. Thus, the reliability and sensitivity of the e-nose system must be investigated and compared with traditional volatile detection techniques in order to determine its ultimate utility.

CHAPTER I

LITERATURE REVIEW

1. Polymer stability

Polymers used for food packaging applications including films, bottles and closures, are composed primarily of high molecular weight molecules, and are considered non-volatile at temperatures below those that induce pyrolysis reactions. However, the production of polymeric packaging materials is often under conditions of high temperature (200-300°C), which can easily induce thermal degradation resulting in the formation of volatile compounds in the packaging materials (Hoff and Jacobsson, 1981; Fernandes et al., 1986). Furthermore, mechanical stress and oxidation during processing may result in polymer chain scission to form precursors of some volatile compounds (Conley, 1970; Ebewele, 2000). Therefore, stabilizers or antioxidants are frequently incorporated into polymer resin at concentrations of 0.01-0.1 weight percent (Calvert and Billingham, 1979) to prevent thermal and oxidative degradation during processing, as well as to prevent polymer embrittlement during storage (Crosby, 1981).

A free radical chain mechanism is generally believed to explain the thermal oxidation of polyethylene as shown in Figure 1. (Bevilacqua et al., 1964; Kelen et al., 1976; Hoff and Jacobsson, 1981; Hinsken et al., 1991; Wessling 2000). Structure, morphology, presence of stabilizers and types of processing environment are the most relevant factors leading to the degradation of polyethylene. Degradation can be initiated by oxygen, shear, heat, catalyst residues or any combination of these factors (Hinsken, et al., 1991).

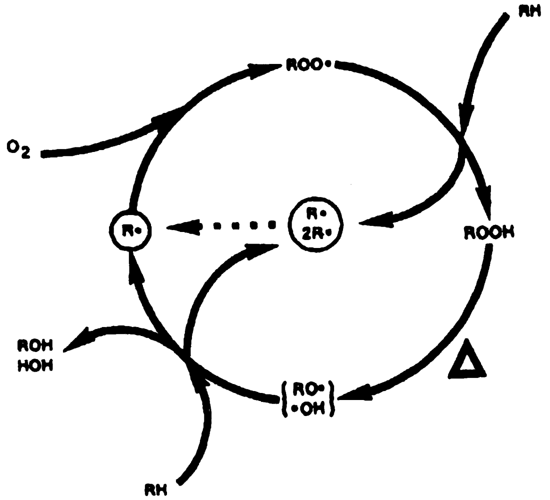

Figure 1 Thermal oxidation cycle of polyolefin (Hinsken et al., 1991)

Free radicals (R•, •OH, •OR) are formed in the initiation step. The R• radicals then react rapidly with oxygen to form peroxyl radicals (ROO•), which may react further with the polymer, resulting in the formation of hydroperoxides (ROOH) and more free radicals (R•) (Figure 1). Hydroperoxides are unstable and can break down to form additional free radicals (RO• and •OH) which will initiate further reaction and propagate the oxidation cycle. Termination of the oxidation cycle can occur when radicals are combined with each other to form non-radical species i.e. recombination of two R• radicals or when antioxidants are introduced (Wessling, 2000). Antioxidants interrupt the cycle by scavenging free radicals, but do not terminate the cycle; once antioxidants are consumed, the process is renewed.

2. Antioxidants

Antioxidants are substances, which are able to inhibit or slow down the oxidation process, by interrupting chain reactions in foods and polymers (Briston and Katan, 1974). Antioxidants prevent oxidative degradation by reacting with free radicals or atmospheric oxygen which would otherwise react with the food or polymer components (Wessling, 2000). An ideal food grade antioxidant should be safe, not impart color, odor or flavor and be effective at low concentration. In addition, it should be easy to incorporate, survive processing and be stable in the finished product, and should be available at low cost (Shahidi and Naczk, 1995).

Antioxidants are able to influence oxidative processes in different ways. Depending on their chemical structure, antioxidants interfere with oxidation by reacting with free radicals, chelating catalytic metals, acting as oxygen scavengers, or by reacting with hydroperoxides (Shahidi and Wanasundara, 1992; Lindsay, 1996; King and Gupta, 1997).

2.1. Role of Antioxidants

There are two major groups of antioxidants which can be distinguished: primary antioxidants or chain terminating and secondary antioxidants or hydroperoxide decomposers (Schwarzenbach, 1984).

Primary antioxidants or chain terminating antioxidants react with radical species (R•, ROO•, RO•, HO•) which are generated in Cycles I and II (Figure 2, King and Gupta, 1997). Most primary antioxidants used in polyolefins are sterically hindered phenols (Ho et al., 1994). This type of antioxidant has a phenol hydroxyl group and an electron releasing substance. The radical scavenging mechanism of a hindered phenol is illustrated in Figure 2. Phenolic antioxidants interfere with oxidation by rapid donation of a hydrogen atom to a free radical, resulting in the formation of a non-radical product (ROH) and a phenoxyl radical. The phenoxyl radical is stabilized by delocalization of unpaired electrons as shown in Figure 3 (Swasey, 1992).

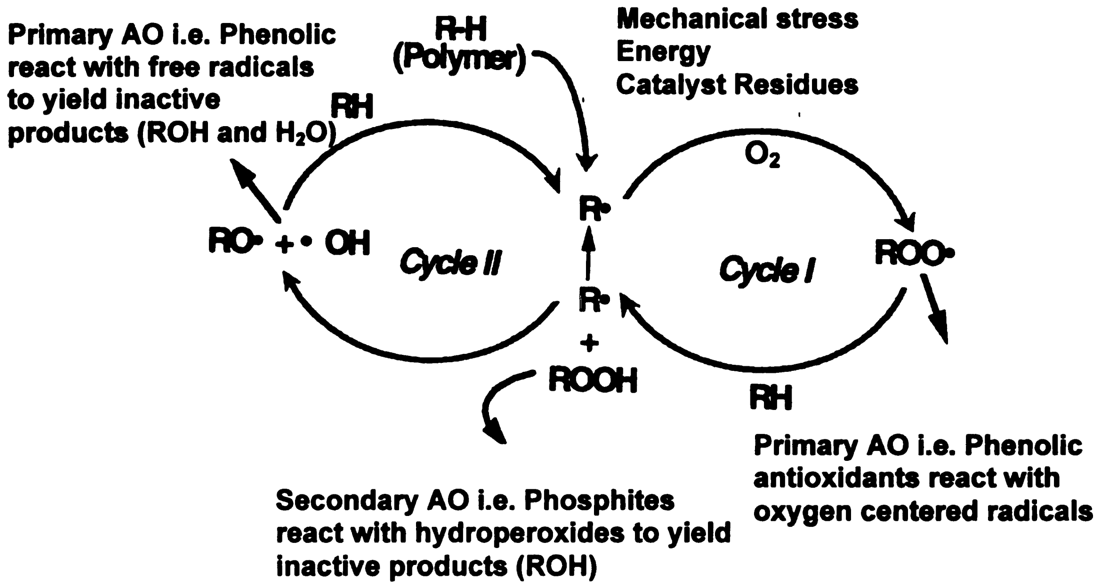

Figure 2 Disruption of the oxidation cycle by primary and secondary antioxidants (AO's) (Revised from King and Gupta, 1997)

Secondary or preventive antioxidants will react with hydroperoxides (ROOH) (Figure 2) to yield non-radical or non-reactive products. The secondary antioxidants are particularly effective in synergistic combinations with primary antioxidants. Phosphites and citrates are examples of secondary antioxidants.

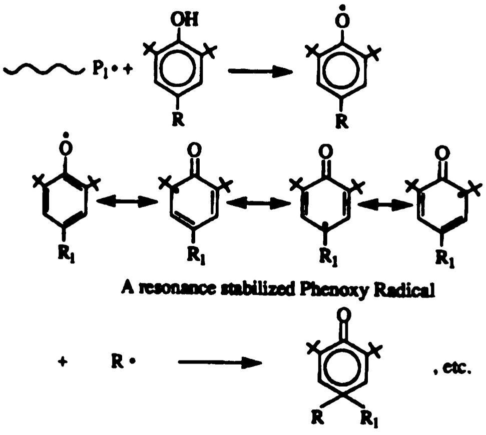

Figure 3 Radical scavenging mechanism and resonance stabilization of phenols (Swasey, 1992)

2. Irganox 1010

Irganox 1010[1] (Pentaerythritol Tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) Propionate]) is a sterically hindered phenolic compound (Figure 4). It is an effective, non-discoloring stabilizer for organic substrates, such as plastics, synthetic fibers, elastomers, adhesives, waxes, oil and fats. Irganox 1010 has good compatibility, high resistance to extraction and low volatility. It is also odorless and tasteless (Ciba® Specialty Chemicals, 1999).

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[1] Trade name by Ciba® Specialty Chemicals (Basel, Switzerland)

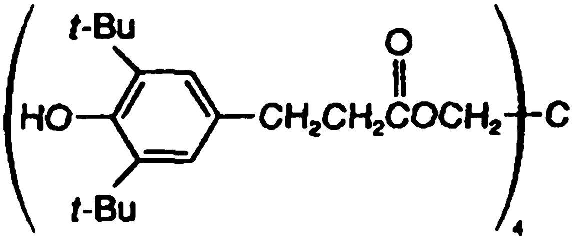

Figure 4 Chemical structure of Irganox 1010

Irganox 1010 is one of the most widely used antioxidants in polyolefin, such as polyethylene, polypropylene, polybutene and olefin copolymers (Foldes and Turcsanyi, 1992). Its compatibility with polyethylene has been reported by several investigators (Roe et al., 1974; Billingham et al., 1981; Foldes and Turcsanyi, 1992).

Schwope et al. (1987) investigated migration of Irganox 1010 and butylated hydroxytoluene (BHT) from low density polyethylene (LDPE) food wrapping material into foods and food-simulating liquids. In comparison to BHT, Irganox 1010 is larger, less volatile and migrates less rapidly into food or food simulating liquids from low density polyethylene than does BHT. Irganox 1010 and BHT have similar performance in reducing the release of volatile compounds from HDPE containers (Yam et al., 1996).

2.3. α-Tocopherol

α-Tocopherol is a natural antioxidant, which can be used to replace synthetic antioxidants. α-Tocopherol is widely used as an antioxidant in food and cosmetic products. In addition, it has been commercially used as an effective melt processing antioxidant for polyolefins, such as LDPE and HDPE (Al-Malaika et al., 1994; Alan et al., 1997; Van Leeuwen et al., 1997).

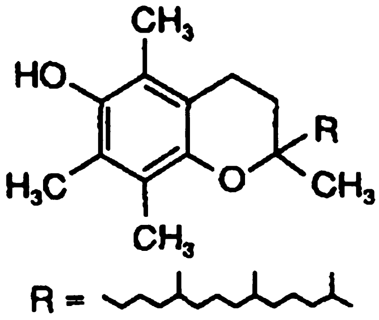

Figure 5 Chemical structure of α-Tocopherol

α-Tocopherol (Figure 5) is the most biologically active form of vitamin E, a fat-soluble, naturally occurring antioxidant (Shahidi and Naczk, 1995; Wessling, 2000). In pure form, α-Tocopherol is a viscous, dark amber oil. It is a safe, non-toxic compound with excellent thermal stability, particularly in the absence of oxygen (Laermer and Nabholz, 1990). The compound and its degradation products (such as tocopherol quinone) are regarded as harmless to humans (Laermer and Nabholz, 1990; Van Leeuwen et al., 1997). α-Tocopherol is generally recognized as safe (GRAS) by the US Food and Drug Administration (Laermer and Zambetti, 1992; Laermer et al., 1996). In addition, it has been approved for use as a food additive in a number of countries, including Canada, Japan, Australia, Korea and all members of the European Community (Lin, 1996).

The chemical structure of α-Tocopherol is similar to many of the hindered phenols used as synthetic antioxidants in polymers. The long alkyl chain imparts excellent solubility in polyolefins, and the antioxidant provides polyolefin resins with excellent thermal and processing stability (Laermer and Zambetti, 1992). As a primary antioxidant, α-Tocopherol reacts with lipid peroxyl radicals by donation of a hydrogen atom to form more stable tocopheroxyl radicals. These can undergo further reaction resulting in non-radical transformation products (Al-Malaika et al., 1994). α-Tocopherol is a very active antioxidant, thus low concentrations can be used. The high activity is partly due to the transformation products, some of which are active as radical scavengers (Van Leeuwen et al., 1997).

Studies have shown that α-Tocopherol provides additional advantages in many specialty applications in food packaging. For example, packaging materials which incorporate α-Tocopherol or vitamin E, improve the shelf life of the contained food products, compared to packaging materials without α-Tocopherol (Laermer and Zambetti, 1992; Zambetti et al, 1994; Lin, 1996; Van Leeuwen et al., 1997; Wessling, 2000). In addition, α-Tocopherol helps to reduce the off-odor or off-taste associated with plastic food packaging materials, such as LDPE and HDPE (Ho et al., 1994; Zambetti et al., 1994; Van Leeuwen et al., 1997). Van Leeuwen et al.(1997) investigated the organoleptic performance of LDPE packaging containing vitamin E for a liquid food. There was a significant improvement in the shelf life of water packed in the LDPE vitamin E impregnated film compared to the LDPE film without vitamin E. Since the formation of low molecular weight volatile compounds from LDPE during processing and aging was suppressed by vitamin E, the taste of the packaged water was of a higher quality for a longer period of time.

2.4. Comparison between Irganox 1010 and α-Tocopherol

Selected properties of Irganox 1010 and α-Tocopherol are presented in Table 1.

Table 1 Properties of Irganox 1010 and α-Tocopherol (Urata, 1988)

Property	Irganox 1010	α-Tocopherol
Molecular weight	1178	430
Melting range, °C	110-125	viscous liquid
Solubility[2], mg/100cm^2		
n-heptane 20°C, 30 days	5.9	4.8
n-heptane 40°C, 30 days	4.0	4.4
Boiling water, 5 min	3.9×10^{-3}	9.1×10^{-3}

Ho et al. (1994) and Yam et al. (1996) demonstrated that α-Tocopherol was effective in reducing off-flavor compounds from HDPE containers, using both

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[2] Test Certificate no. 4057-4059, Japan Foods Oils & Fat Test Association

sensory evaluation. Container material which contained α-Tocopherol had lower off-odor intensity and higher acceptability than the containers with Irganox 1010 or BHT. A commercial scale study of off-flavor release from HDPE containers was conducted by Ho and Yam (1997). The sensory results showed that HDPE containers incorporating α-Tocopherol had less off-flavor than packages containing other commercial antioxidants including Irganox 1010.

The effect of α-Tocopherol and Irganox 1010 on melt stability of multiple extrusion polyolefins has also been investigated. Laermer and Zambetti (1992) studied the melt stability of multiple extrusions of HDPE at 205-210°C. When compared to Irganox 1010, Irganox 1076 (Octadecyl 3, 5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate) and BHT, 100 ppm (wt/wt) of α-Tocopherol compared quite favorably with these commercial antioxidants. Al-Malaika et al. (1994) evaluated multiple extrusions of LDPE at 180°C, and found that LDPE containing α-Tocopherol exhibited slightly better melt stability than LDPE containing Irganox 1010, especially at low concentration and under severe processing and reprocessing conditions. In addition, the melt stability effect of α-Tocopherol was found to be much higher than Irganox 1010 (Al-Malaika, et al., 1999).

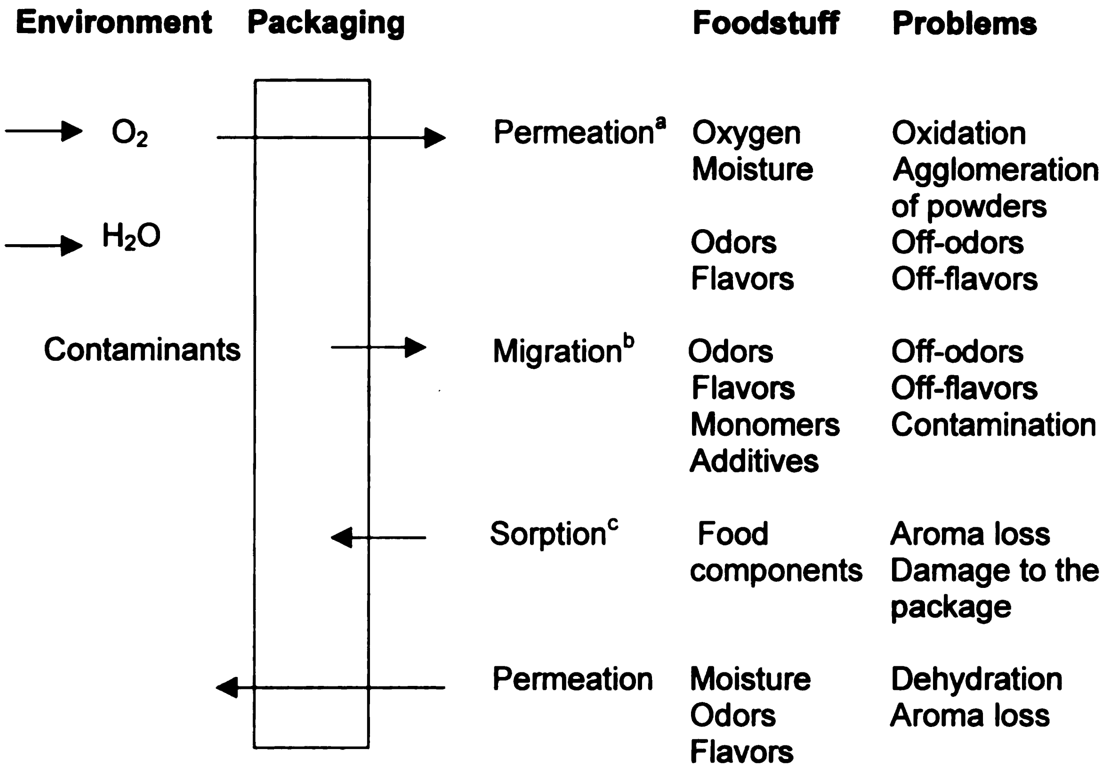
Urata (1988) studied the effect of BHT, Irganox 1010 and α-Tocopherol on polymer stability during multiple extrusion molding using polypropylene (PP) resins. The results showed that α-Tocopherol had better stability than BHT and Irganox 1010. The heat resistance of each stabilizer was also determined. α-

Tocopherol had a lower tendency to decrease in weight than BHT, and had a higher tendency compared to Irganox 1010.

Development of a yellow color in both resins and containers is a major disadvantage associated with α-Tocopherol. Laermer and Zambetti (1992) found that Irganox 1010 provided better color stability in HDPE containers than α-Tocopherol. Similar results were also reported by Urata (1988), Ho and Yam (1997) and Al-Malaika et al. (1999), who found that α-Tocopherol contributed more to the yellow color formation in HDPE or PP resin pellets than Irganox 1010. An increase of discoloration was due to an increase of tocopherol level (Al-Malaika et al., 1999).

3. Interactions between plastic materials and food products

Plastic packaging materials are widely used for food products since they have many advantages over other materials, namely durability, flexibility, lightweight and low cost. However, plastics are not inert and are not perfect barriers, and may interact with packaged food products. The following interactions may occur between plastic materials and contained food products (Figure 6).



a. Permeation, the transfer of components such as odors, flavors or vapors through the packaging material in either direction.
b. Sorption, the transfer of food components to the packaging material.
c. Migration, the transfer of packaging components into the food.

Figure 6 Interactions between food and packaging materials

(Revised from Wessling, 2000)

3.1. Off-odor from plastic packaging materials

Plastics in contact with food should not contribute to the organoleptic properties of the food. If the organoleptic properties of the food are changed in any way, the result is almost invariably considered unfavorable; if the change is sufficiently unpleasant, the result is called 'off-odor' and 'off-flavor' or 'tainting'

(Briston and Katan, 1974). Sources of off-odor or off-flavor compounds include residual monomers and oligomers, residual solvents from printing inks, adhesives and coatings, breakdown products of polymers, and specific additives. These volatile compounds can transfer to contained food products, which causes concern due to safety and consumer perception of quality. Thus, effective quality control is required to avoid off-odor development during production, as well as to minimize the level of trace contaminants, which can transfer from packaging materials.

Goldenburg and Matheson (1975) reported a "catty" flavor in fruit drinks packaged in polyvinyl chloride (PVC) bottles. A metal stabilizer was added to the PVC resin. It contained mercaptide groups that were split off during molding, resulting in an undesirable flavor that migrated into the fruit juice. The use of a stabilizer without mercaptide groups eliminated the problem.

Dicholoromethane is used as a solvent in the manufacture of polycarbonate (PC), and small amounts of it may remain in the resin following polymerization. An automated headspace analyzer was used to determine the amount of residual dichloromethane in the polycarbonate resins. The level of residual dichloromethane detected ranged from 1-100 ppm (wt/wt) (DiPasquale et al., 1978).

Vaccaro (1980) identified several volatiles from polyethylene terephthalate (PET) coated paperboard released during microwave heating. When the paperboard and PET films were analyzed separately to establish the origin of the released volatiles, none could be associated with the PET film. Eight compounds were identified from the paperboard: acetone, 2,3,-butadione, chloroform, furan, furfural, methylene chloride, carbon disulfide, and acetaldehyde.

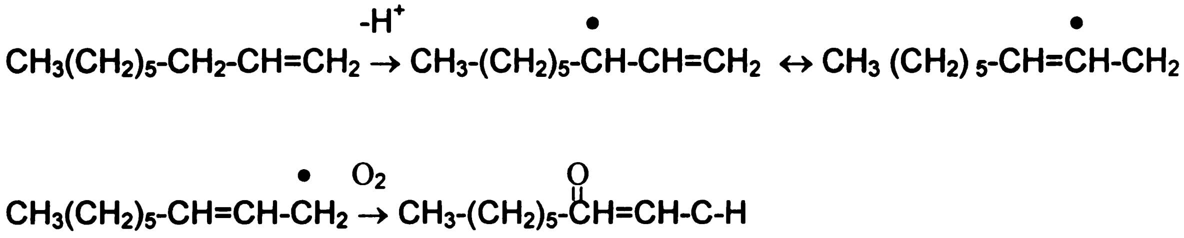
Passey (1983) investigated an off-flavor problem with chocolate and lemon cream cookies packaged in polystyrene trays, and wrapped with printed cellophane. Both organoleptic and gas chromatographic analysis showed that the styrene monomer from the polystyrene trays was the culprit. The level of residual monomer in the trays was determined to be 0.18 to 0.20% (wt).

3.2. Off-odor from polyethylene

Polyolefins, such as polyethylene (PE) and polypropylene (PP) are often processed into packaging materials at high temperatures in the presence of oxygen and with substantial shear stress. This can result in oxidative and thermal degradation of the polymer to form residual by-products (Kim-Kang and Gilbert, 1989). Thermooxidative reactions in polyolefins can cause the development of adverse flavors that are easily detected in degraded polymer samples (Ho et al., 1994; Hinsken et al., 1991).

Polyethylene (PE) is formed by polymerization of ethylene. Low density polyethylene is produced using a very high pressure and high temperature process, but high density polyethylene is produced at low pressure and temperature. Since the process to make HDPE is less vigorous, there are fewer, and shorter branch chains than LDPE. The molecules are practically linear, which allows them to pack closely together. Therefore, its crystallinity and density is high. The density of HDPE ranges between 0.941 – 0.965 g/cm^3 and higher, while the density of LDPE is approximately 0.910 – 0.925 g/cm^3. HDPE is stiffer and has better barrier properties than LDPE (Hanlon, 1992).

Generally, low density polyethylene (LDPE) tends to degrade to shorter chain hydrocarbons at temperatures greater than 300°C and can undergo further oxidation to form a large number of oxidative products such as aldehydes and alcohols (Hoff and Jacobsson, 1981). Koszinowski and Piringer (1983) investigated the off-odor substances in polyethylene packaging materials by splitting of the GC effluent between a sniffing port and a mass spectrometer. The authors concluded that two important odor substances, 1-hepten-3-one and 2-nonenal, were sometimes found in polyethylene packaging materials. Trace levels of 1-nonene (ppm range) were found in low density polyethylene (LDPE). The material was oxidized, probably by a free radical mechanism in the allylic position, to 2-nonenal, as shown below;



$$CH_3(CH_2)_5\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{-H^+} CH_3\text{-}(CH_2)_5\text{-}\overset{\bullet}{C}H\text{-}CH{=}CH_2 \leftrightarrow CH_3\ (CH_2)_5\text{-}CH{=}CH\text{-}\overset{\bullet}{C}H_2$$

$$CH_3(CH_2)_5\text{-}CH{=}CH\text{-}\overset{\bullet}{C}H_2 \xrightarrow{O_2} CH_3\text{-}(CH_2)_5\text{-}\overset{\overset{O}{\|}}{C}H{=}CH\text{-}C\text{-}H$$

Bravo et al. (1992) used gas chromatography/olfactometry to identify 14 odor-active compounds from thermal oxidation of polyethylene at 250°C for 15 min. Most of these compounds occurred in amounts too low to be detected instrumentally. Approximately 46% of the aroma resulted from hexanal, heptene-

3-one, 1-octen-3-one, octanal, 1-nonen-3-one, nonanal, trans-2-nonenal and diacetyl. α-unsaturated aldehydes and ketones were responsible for much of the off-odor associated with the thermally oxidized product. Unfortunately, the above studies were limited only to thermal oxidation, which is not representative of real processing conditions where shear effects must also be considered.

Hoff and Jacobsson (1981) identified 44 volatiles from thermal-oxidative degradation of low density polyethylene at 264-289°C using GC-MS analysis. Compounds identified included hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, cyclic esters and hydroxy carboxylic acids. Fatty acids and aldehydes predominated among the compounds identified.

Bravo and Hotchkiss (1993) studied the release of volatile compounds during heating of polyethylene in the presence of oxygen at 150-350°C for 5-15 min. 84 volatile compounds in the range of C_5-C_{23} were identified. The major products were aliphatic hydrocarbons, aldehydes, ketones, olefins, and hexanal. The amount and type of compounds produced were affected by temperature and heating time.

The potential contribution of polyethylene packaging to dairy product off-flavors was evaluated by Foissy (1979) utilizing GC-MS in parallel with organoleptic tests. The flavor compounds identified included isomers of N,N-dimethyl-p-toluenesulfonamide, dibutylthiophene, myristic acid, palmitic acid, traces of C_8-C_{23} saturated fatty acids, lauric acid, butoxyethanol, butanol, hexanol, diethyleneglycol and butoxypropanol.

Polyolefins can develop a wax-like odor if the package is overheated (Brody, 1989; Kim-Kang, 1990). Koszinowski and Piringer (1983) indicated that different odor characteristics could originate from polyethylene (PE) depending on odor substances present and the number of carbon atoms in the backbone, as shown in Table 2. The threshold levels of some of the odor substances found by Koszinowski and Piringer (1983) are shown in Table 3.

3.3 Selective HDPE off-odor compounds

High density polyethylene (HDPE) is one of the most versatile polymers used for packaging (Jenkins and Harrington, 1991) and can be readily converted to film, sheet and containers. It is the most widely used of the three basic types of polyethylene resins in the United States. In the year 2000, approximately 7.1 million tons of HDPE resins were supplied in the US and Canada (Modern Plastics, February, 2001). Blow molding is used to convert HDPE resin into bottles.

Polyethylene is relatively inert and a good barrier to moisture (Paine and Paine, 1992). In most applications, it is essentially tasteless and odorless (Hanlon, 1992). HDPE is approved for use in contact with food, since it meets the requirements under regulation CFR121.2501. Use of antioxidants is essential to prevent degradation during processing of HDPE (Briston and Katan, 1974; Billingham and Calvert, 1981; Yam et al., 1996).

Table 2 Odor characteristics of some unsaturated oxidative compounds

No. of carbon	**1-Alken-3-ol (Alcohols)**	**1-Aken-3-one (Ketones)**	**1-Alkenal (Aldehydes)**
5	Benzene	Leek	-
6	Smoked fish, Sweat	Pungent, Leek, Sweat	Almond oil, Green
7	Pungent, Smoked fish, Sweat	Pungent, Leek, Plastic-like (Polyolefin)	Almond oil, nut, rancid
8	Mushroom-like	Mushroom-like	Rancid, Brazil nut, Musty
9	Humus, Mushroom-like	Humus, Mushroom-like	Beg bug, Musty
10	Cleaning agent, soapy	Bitter, Fruit, Plastic-like (Polyolefin)	Unpleasant, Soapy, Rancid, Musty
11	Cleaning agent, soapy	Fresh, Bitter, Fruity-like	Soapy, Mandarin peel, Flowery-like
12	Tomato, Vegetable, Soapy	Fresh fruit; Apple	-
15	Vegetable, Bean, Pea	Fresh, Bitter, Fruity, Moldy cheese	-

Table 3 Threshold level in ng and in mg/m^3 air of selected volatile compounds with n C- atoms (n = no. of carbon in backbone)$^{(a)}$

N	1-Alkene		1-Alken-3-ol (Alcohols)		1-Alken-3-one (Ketones)		2- Alkenal (Aldehydes)	
	ng	mg/m^3	ng	mg/m^3	ng	mg/m^3	ng	mg/m^3
5	-	-	900	0.66	28	0.02	-	-
6	-	-	100	0.07	1	0.0007	45	0.033
7	50,000	37	100	0.07	0.9	0.0007	45	0.033
8	50,000	37	150	0.11	0.15	0.0001	9	0.007
9	50,000	37	60	0.04	0.025	0.00002	1.6	0.001
10	50,000	37	500	0.37	1.5	0.001	11	0.008
11	-	-	500	0.37	1.5	0.001	18	0.013
12	-	-	5000	3.7	250	0.18	-	-
15	-	-	200,000	150	4000	2.9	-	-

$^{(a)}$ *Threshold levels determined by gas chromatography analysis*

There are three possible predictors that can be used to determine the contribution of individual compounds to the release of odor, namely: odor threshold, molecular weight and polarity (Ho et al., 1994). The lower the sensory threshold the more readily the odor can be detected. In this regard, aldehydes and ketones are of particular concern as they have odor thresholds at least 3 orders of magnitude lower than those of alkanes and alkenes (Koszinowski and Piringer, 1986).

An important consideration with respect to molecular weight is how rapidly the odor compounds desorb from the polymer matrix to the gas phase. For a homologous series, the lower the molecular weight, the more volatile the odor compound. Low molecular weight compounds such as C_4-C_5 olefins easily volatilize to the gas phase during the blow molding process and, therefore, should not be found in the polymer matrix (Ho et al., 1994).

Polar volatiles also have a higher propensity to volatilize or desorb from a non-polar polymer matrix. The most offensive odor compounds from HDPE produced during the blow molding process may be those ketones or aldehydes of a certain molecular weight range which are not volatile enough to flash off during the blow-molding process, but yet are sufficiently volatile to desorb from the polymer matrix during storage. Among all the aldehydes, nonanal is likely a major contributor of the off-odor from HDPE because of its abundance, low odor threshold and low molecular weight (Yam et al., 1996).

Some ketones, and particularly 1-hepten-3-one, were reported by Koszinowski and Piringer (1983) and Bravo et al. (1992) to be the predominant odor active compounds produced from thermal oxidation of polyethylene. Ho et al. (1994) could not detect 1-heptene-3-one by GC-MS analysis of a HDPE headspace sample. Reports which identified this ketone as an odor active substance were based on Charm analysis and other instrumental techniques. Thus, ketones and especially 1-hepten-3-one are not suitably selective compounds to use to monitor off-odors from HDPE, based on GC-MS analysis.

Ho and Yam (1997) conducted a commercial scale study of off-flavors from HDPE bottles containing vitamin E using sensory and GC-MS analysis. The authors identified more than 55 volatile compounds in the range C_6-C_{20}, with molecular weights ranging from 80-300. The compounds belonged to a group of n-alkanes, 1-alkenes, aldehydes, ketones, phenols, and other alkanes and alkenes. The most abundant group was 1-alkene, which contributed more than 50% of the total volatile compounds. The results agree with those of Ho et al. (1994) and Yam et al. (1996) who showed that alkanes and alkenes made up a significant portion of the thermal/mechanical degradation fragments of polyethylene.

Ho et al. (1994) also reported the effect of blow molding on generation of volatiles during HDPE fabrication. The authors found that concentrations of paraffin, olefin and especially n-alkane increased, while the 1-alkene concentration decreased during container fabrication. The aldehyde and ketone concentrations remained almost unchanged, if HDPE pellets containing 100 ppm vitamin E were used. Concentrations of n-alkanes, aldehydes and ketones increased when HDPE pellets were mixed with 500 ppm Irganox 1010. In both cases, the total volatile concentration increased mainly due to an increase in n-alkanes.

3.4. Off-odor problem in drinking water

Consumers are drinking more bottled water than ever before. According to recent statistics, consumer demand for bottled water has increased by a factor of three in the last decade (Olson et al., 1999). Sales of bottled water increased 13.9% in 1999 to $5.2 billion (International Bottled Water Association, 2001). Even though it costs consumers 240 to over 10,000 times more per gallon than tap water, more than 50% of people in the US drink bottled water, and approximately, one-third of consumers drink it regularly (Olson et al., 1999). Consumers choose bottled water for its clean, refreshing taste, and as an alternative to beverages with calories, sugar or caffeine (Le, 1996).

The Food and Drug Administration has defined bottled water as water that is sealed in bottles or other containers and is intended for human consumption (FDA, 1996). It is fully regulated as food under the Federal Food, Drug, and Cosmetic Act (FFDCA) 21 U.S.C. § 301*et seq*. The FFDCA defines food as "articles used for food or drink for man or other animals...." FFDCA § 201(f). This includes packaged water sold in small containers at retail outlets as well as larger containers distributed to the home and office market. Bottled water is subject to FDA's extensive food safety and labeling requirements. In addition, bottled water is one of only several food product categories that is subject to additional specific FDA Good Manufacturing Practice ("GMP") requirements (Figure 7).

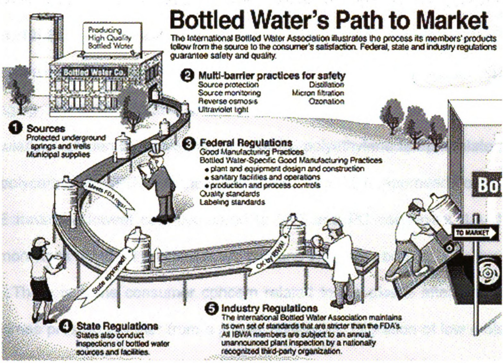


Figure 7 Bottled water's path to market
(http://www.bottledwater.org/public/BWFactsHome_main.htm)

Off-odor or off-flavor problems can come from the water source or processing plants, as well as packaging materials. Water can come from natural underground springs, wells or municipal supplies. Treatments such as filtration, distillation etc., may be used depending on the water source (Wayman, 1998; Olson et al., 1999). More than 50% of bottled water sold in the US comes from municipalities (FDA, 1996). The taste of tap water varies depending on location and how the water has been treated or processed. Environmental contamination also has an effect on the taste of tap water. Chlorine is one of the most commonly perceived tastes associated with municipal water and the chemical imparts a slightly acidic taste. Water impurities such as chlorine and other chemicals can affect the taste of many foods and beverages (Ashurst and Senior, 1998).

Drinking water bottles come in various shapes and sizes. Typical packaging used for bottled water includes glass and plastic containers, particularly, high density polyethylene (HDPE), polyethylene terephthalate (PET) and polycarbonate (PC). Containers made from FDA approved food grade HDPE have the lowest cost compared to PET and PC containers (Le, 1996). Common sizes of HDPE containers are one and 2.5 gallon bottles.

There is some consumer concern related to the plastic aftertaste that is sometimes present in water from a plastic container. Migration of low molecular weight compounds from the bottle material into water has been reported by several authors. For example, Crompton (1979) reported that an increase in pH and total solids in water may be due to migration of polymeric residues, non-polymeric additives and adhesive compounds from packaging materials. Migration of polymeric additives may contribute to the development of plastic odor and taste (Shepherd, 1982).

Olson et al. (1999) identified some volatile compounds from bottled water sold in California, Florida, New York, Illinois and Texas in 1994. The results showed that di-2-ethylhexyl phthalate (DEHP) was found in 3% of water packaged in PET containers.

Page et al. (1993) identified the volatile organic compounds present in bottled water sold in Canada. 182 samples of commercial bottled water which were packaged in glass and plastic containers, such as polyethylene terephalate

(PET), high density polyethylene (HDPE), polyvinyl chloride (PVC) and polycarbonate (PC) were investigated. The authors found cyclohexane contamination in 20 of 37 HDPE bottles containing spring water. The average level of cyclohexane found was 42 ppb. In addition, they found cyclohexane contamination in three mineral and other water samples packaged in HDPE. Further analysis by the investigators indicated that packaging was the source of contamination since cyclohexane is used in plastic manufacturing.

The above investigators also found pentane at a level of 19 ppb in the bottled spring water (Page et al., 1993). Pentane is used as a blowing agent to make polystyrene foam, which is sometimes used as a cap liner. Vinyl chloride contamination in water packaged in PVC bottles was investigated by Benfenati et al. (1991). They found that levels of vinyl chloride monomer in bottled water increased after storage and were proportional to storage time.

Le (1996) stated that the plastic taste intensity associated with HDPE containers depends on the quality of the blow molding process and storage conditions. The plastic-like taste of water in HDPE bottles can be the result of one or more of the following:

- Bottles stored longer than one year.
- Bottles stored at temperatures higher than 49°C (120°F) for more than 72 hours.
- Contaminated air supply to the blow molding machine or melting temperature greater than 204°C (400°F)

- Short machine cycle time: less than 8 seconds for 4-head machine, less than 9 seconds for 6-head machine.
- Presence of high level of oxidation products, e.g. aldehydes, ketones and acids, in the process stream during production of raw HDPE resins.

The bottled water market is growing rapidly. The average growth rate is 8-10% per year (Olson et al., 1999). The consumption of bottled water has increased. Consumers expect high quality water. After a worldwide recall of Perrier mineral water due to benzene contamination in February, 1990, both government and private sectors paid more attention to the quality of bottled water (Anon, 1996; Ashurst and Senior, 1998; Olson et al., 1999). To ensure container integrity, packagers need to be aware of quality issues at both the bottle manufacturer's facility, where the complexity of molding operations requires a good preventive maintenance program, at the water bottling plant. Thus, rapid analysis techniques should be established in order to guarantee the high quality of bottled water.

4. Analysis of off-odor from packaging materials

Polymeric packaging materials are of such diverse composition that the precursors for volatile compounds can be derived from many sources. These can include residual monomers and oligomers, residual solvents from printing inks, adhesives, coatings, breakdown products of polymers, and specific additives. Therefore, precautions have to be taken to avoid off-odor development during production, as well as during packaging, by effective quality control. The packaging converter should be able to manufacture the packaging in such a way as to reduce the level of trace contaminants which may transfer from packaging materials to contained food products.

The measurement of taste and odor is a complex process. Although consumers usually report taste as the cause of the problem, it is more likely that they have in fact perceived an odor (Baker, 1966). Taste is referred to as a result of taking a sample into the mouth, whereas odor refers to the result of assessing a sample by smelling (Young et al., 1996).

Taste and odor problems associated with polymers have historically been difficult to evaluate subjectively and objectively, particularly when low amounts of odor active substances are present. While it may naturally be assumed that those products with an unpleasant taste or smell are not safe to consume, there are many examples where that is not always true. Some chemicals may be detected sensorily at concentrations far below analytical detection limits. Conversely, the absence of flavor effects does not guarantee the absence of undesirable contaminants (Young et al., 1996).

4.1. Sensory analysis

Foods must be safe, but also of high sensory quality. Sensory attributes are critical in the public perception of drinking water quality (MacRae and Falahee, 1995). Peled and Mannheim (1977) determined off-flavor in milk samples using sensory and analytical techniques. The investigators concluded that organoleptic tests were the most reliable tests for determination of the off-flavors originating from packaging.

The odor quality of polymeric materials, such as resins, films or laminates, can be estimated directly by sensory panelists using a rating scale evaluation of intensity, or by forced choice methods such as the triangle test and paired comparison (Kim-Kang, 1990; Thompson et al., 1994; Le, 1996). The extent of migration of residual volatile compounds in packaging materials to the contacting phase can be evaluated after exposure to water, to a food stimulant, or by exposure of an actual food to packaging materials at accelerated conditions, at ambient temperature, or at actual cooking conditions.

For example, Kuijk and Warnar (1993) investigated the organoleptic properties of an extrusion coating LDPE cast film. A paired comparison test was performed using 15 trained panelists. Approximately 1.6 g of film samples were cut into small pieces of 1 x 1 cm and placed in a glass bottle containing 1 L of tap water. After 24 hours at 23°C, the water sample was diluted with fresh tap water and served to the trained panelists.

Sensory evaluation can be paired with objective instrumental analysis and a correlation between the sensory and instrumental results can be obtained. Organoleptic analysis works better than instrumental analysis, since some off-flavors can be detected by taste but cannot be measured instrumentally. Sensory panels can detect an odor or flavor at much lower concentrations than the usual chemical techniques (Peled and Mannheim, 1977; MacRae and Falahee, 1995). Fales et al. (1983) correlated resin odor with GC-MS analysis by plotting major peak areas against overall odor intensity. However, the aroma was not separated into its individual components and specific odor active compounds were not identified.

A degree of difference test was developed to replace the traditional triangle and duo-trio test for products (Aust et al., 1985). The difference-from-control test is useful where there is a difference between the samples and the size of the difference affects the decision making related to the test objectives. One sample is designed as a control or reference and all others are evaluated with respect to how different each sample is from the control, i.e. no difference, slight difference, significant difference. The panelist is also asked to evaluate a blind control, which is not different from the control or reference (Meilgaard et al., 1991; Thompson, 1998).

Aust et al. (1985) evaluated the performance of the difference test method compared to the triangle test using heterogeneous products such as deviled ham, chili, vienna sausage, sloppy joe, pizza and beef stew. The results showed that the use of the triangle test with a highly variable product results in a high frequency of false statistically significant results.

Panelist training is also important for taste and odor evaluation since it will increase sensitivity of the sensory panels to a range of compounds and will improve the performance of the sensory panel (MacRae and Falahee, 1995). For each flavor or odor, detection is assumed to occur when the intensity of the stimulus exceeds the threshold. If the flavor is detected, the correct response is made. If it is not detected, the panelist randomly guesses with a low probability of being correct.

Sensory evaluation of drinking water

Several sensory techniques and testing conditions have been used to detect off-taste or off-odor in drinking water. For example, Van Leeuwen et al. (1997) determined the organoleptic properties of drinking water stored in LDPE cast film with and without vitamin E. A paired comparison test was performed using 10 trained panelists. The water samples were prepared by adding film to tap water (6.0 g/L) in 0.5 L glass bottles. The water was treated using a Millipore filter system to remove organic components and microorganisms. The bottles were stored at 40 ± 2°C for 49 weeks with sampling at 0, 3, 6, 12, 18, 24, 36 and 49 weeks. The reference samples were made from freshly prepared films incubated in water (6.0 g/L) at 40 ± 2°C for 24 hours before being served to the taste panel.

Nadanasabapathy et al. (1995) evaluated the organoleptic attributes of potable water packaged in laminated and co-extruded films stored at ambient (26-32°C, 65%RH) and high temperature conditions (37°C, 90%RH). The organoleptic properties of potable water packaged in paper/Al foil/LDPE, PET/Al foil/LDPE, metallized PET/HDPE, HDPE/LDPE and glass bottles were determined using a 9-point hedonic scale by 7 trained panelists. The water was pasteurized at 80°C for 5 min. Approximately 150 ml water at the ratio of 1 ml/cm^2 surface contact area was filled into the above packaging materials and stored at ambient and accelerated conditions.

Linssen et al. (1991) evaluated taint in water packed in LDPE/ aluminium pouches using sensory descriptors. Test pouches were made from LDPE extruded onto aluminium, immediately folded and sealed into a pouch. The test pouches were filled with 250 ml water and incubated at 40°C for 24 hours. 48 untrained assessors were asked to taste and characterize the water by their own expression. The panel agreed on eight descriptive attributes; metallic, synthetic, dry, rough, astringent, musty, sickly and penetrating. Further, 14 trained panelists were selected to participate in an intensity test from the selective descriptive attributes.

A taste test and an odor test were conducted by Ho et al. (1994) to evaluate the organoleptic properties of HDPE containers produced using vitamin E, Irganox 1010 and BHT as antioxidants using 32 untrained panelists. Water samples were obtained from a local supermarket. 3.5 L of water was filled in the HDPE containers and stored in an environmental chamber at 38 ± 1°C, for 4 days. After 1 and 4 days, the bottles were removed from the chamber and were equilibrated to room temperature before the water was served to the panelists. A duo-trio test was performed to evaluate taste. To evaluate odor, the panelists opened and sniffed the headspace in the sample. The panelists were asked to express their responses on a 15 cm line scale, where 0 was no detectable odor and 15 represented strong detectable odor.

4.2. Instrumental analysis

The most popular instrumentation for the identification of unknown volatile compounds include: (i) gas chromatography/mass spectrometry (GC-MS); (ii) electron impact (EI), chemical ionization (CI), mass spectrometry–mass spectrometry (MS-MS); and (iii) gas chromatography-infrared spectroscopy (GC-IR).

Headspace gas chromatography is one of the most widely used techniques to identify trace levels of volatile compounds (Nitz, 1987). Kim-Kang (1990) reported that headspace gas chromatographic techniques were used as a rapid method for the tentative identification of volatile contaminants. However, due to the limited amount of headspace gas that can be injected into the gas chromatograph (GC), low sensitivity is a problem with this method (Hartman et al., 1993). The detection threshold capabilities of GC detectors and mass spectrometers (MS) prevents detection of trace levels of flavors often present in the headspace, although these same compounds are often organoleptically significant at these low concentrations. The injection of large amounts of headspace gas into the GC results in loss of chromatographic resolution. Thus, enrichment techniques collectively called dynamic headspace analysis have been developed. These techniques involve a means of concentrating headspace aroma volatiles prior to GC analysis.

Dynamic headspace/gas chromatography (DH/GC) has gained popularity as an effective and sensitive technique for the analysis of volatile compounds. This technique involves the use of a porous polymer sorbent trap and direct thermal desorption. Vapor samples can be prepared by drawing the headspace of sealed packages through trapping tubes containing an adsorbent. Trapping media such as Tenax-GC [poly (2, 6- diphenyl-p-phenylene oxide)], activated carbon, and silica gel have been developed and are used to enhance the capability of this technique (Hartman et al., 1993).

Depending on the application, the type of sorbent material used is also an important factor in the thermal desorption technique. The pore diameter and particle size distribution of activated carbon profoundly influences the breakthrough volumes of various analytes, with smaller particles and pores being more efficient for trapping highly volatile low molecular weight hydrocarbons such as C_2 - C_4. Silica gel has a problem with trapped water. Thus, commercially available absorbent traps offer a mixed bed design with any number and combination of adsorbents to improve their trapping efficiency.

The purge and trap, or dynamic thermal desorption (P&T-TD) technique involves the sparging of a solid or liquid sample with a purified inert carrier gas to purge headspace volatiles onto an adsorbent trap. The vapors concentrated in the adsorbent trap are subsequently released by thermal desorption (TD) and transferred directly to a gas chromatograph (Figure 8) for analysis (Hartman et al., 1993). This procedure has a significant increase in sensitivity relative to static headspace measurements.

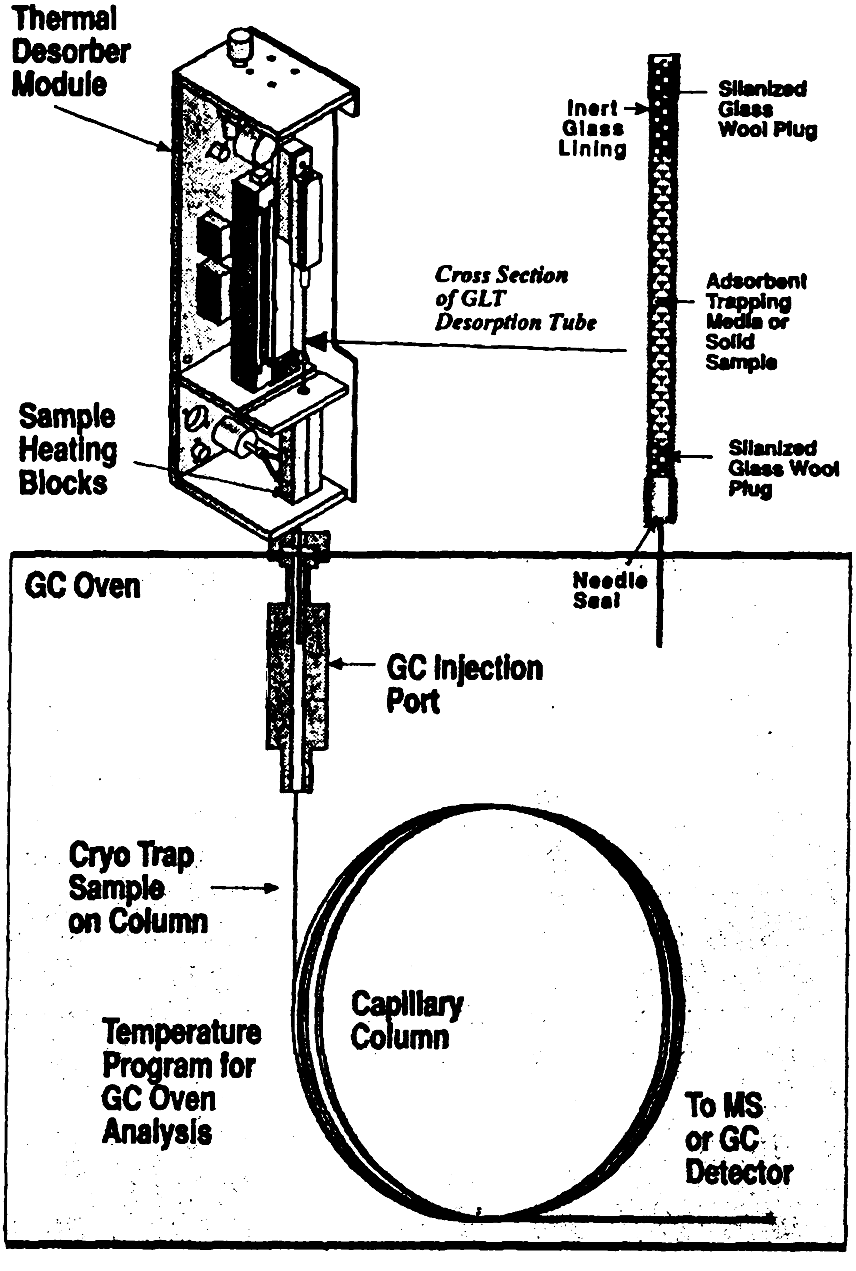


Figure 8 A short-path thermal desorption module mounted on a gas chromatograph (Hartman et al., 1993)

Brunner et al. (1978) compared thermal desorption and solvent extraction techniques. The authors reported that thermal desorption methods have advantages over solvent extraction techniques. For example, they offer higher sampling flexibility, more homogenous behavior to different substances and higher overall sensitivity. Imhof and Bosset (1994) used dynamic headspace analysis with GC-MS to identify and quantify the volatile compounds in pasteurized milk and fermented dairy products. The authors concluded that the dynamic headspace method provides an accurate analysis of the volatile compounds in milk.

Hartman et al. (1993) also used a purge and trap thermal desorption method with GC-MS analysis. BHT and trace levels of halogenated hydrocarbons were found in a raspberry-flavored carbonated beverage packaged in a PET container. The authors indicated that BHT most likely migrated from the container to the product, but that low ppb levels of halogenated hydrocarbons were common impurities in water used to formulate the beverage.

Vercelloti et al. (1987) used a purge and trap procedure, combined with GC-MS, for comprehensive analysis of nitrogen, oxygen and sulfur-containing volatile compounds in ground roast beef, commercial beef flavor concentrate, and beef meat powder. The volatile compounds were trapped on a Tenax material containing a glass lined trap. The trap was later heated and volatiles purged into a GC-MS system for identification and quantification. They were able to identify more than 50 heteroatomic, mostly cyclic compounds. Sabio et al.

(1998) also used a dynamic headspace technique coupled to GC-MS analysis to compare volatile compounds released from dry cured ham.

Analysis of flavor volatiles in tomato and strawberry fruits using GC and time-of-flight MS (TOFMS) with solid phase microextraction has been reported (Song, et al., 1998). The investigators concluded that the major volatile compounds detected, and their relative abundance were comparable to published results from purge-and-trap GC-FID analysis.

Instrumental analysis of water samples

Instrumental analysis of trace organic compounds in water requires a very sensitive analytical procedure because of the low concentrations at which these organic compounds occur. Thus, the analytical method requires an ability to detect very low levels and a high discriminatory capability. Gas chromatography-mass spectrometry (GC-MS) with selected ion monitoring (SIM) is the most widely used method for the determination of taste and odor compounds in drinking water (Hwang et al., 1984; Korth et al., 1991; Kelly et al., 1993).

Purge and trap thermal desorption and/or thermal stripping techniques are commonly used for analysis of low (ng/L) levels of non-polar, volatile organic compounds of intermediate molecular weight in water (Boren et al., 1982; Boren et al., 1985; Savenhed et al., 1983; Kristiansen et al., 1993). The volatile organic compounds are stripped from the water sample by a recirculating stream of air. The organics are removed from the gas phase by trapping on a porous sorbate, such as activated carbon. Subsequently, the compounds are released by thermal desorption (TD) with transfer directly to a gas chromatograph for analysis.

An alternative to GC-FID and GC-MS is the use of a table-top MS system, i.e. the Hewlett Packard mass selective detector (MSD). A GC-MSD is much less expensive than a research model GC-MS system and has been used successfully at the Canadian Metropolitan for routine analysis of 2-methyl isoborneol (MIB) and geosmin in complex water samples (Kraner, 1988). To achieve a ppb level sensitivity the MSD must be run in a selected ion monitoring (SIM) mode. However, it is important to run more than one ion per compound to avoid false identification of a target compound from closely eluting compounds.

Use of a purge-and trap GC-MS with selected ion monitoring (SIM) is also recommended instead of a full scan, since the concentration of the volatile compounds by a purge-and trap method is less sensitive than closed-loop stripping analysis. However, this limitation precludes the full-scan mass spectral identification of the volatile and non-volatile compounds present in a sample.

Skjevrak (1998) identified volatile organic compounds (VOC) in drinking water using a purge and trap procedure with modified Tenax adsorbents accompanied by automatic thermal desorption of VOC and GC-MS analysis

Van Leeuwen and Kuijk (1997) used a GC-MS stripping technique to evaluate volatile compounds migrating from LDPE cast film samples. 0.5 L of water was put into a 1 L Erlenmeyer flask equipped with a special glass frit. For the stripping procedure, the flask was heated at 60°C for 3 hours with 50ml/min of helium flow. The volatiles were trapped on Tenax TA at ambient temperature and desorbed at 250°C for 15 min before analysis using GC-FID interfaced with the Mass Selective Detector (MSD).

4.3. Electronic olfactory sensing technology

An aroma profile may consist of hundreds of different odorous molecules. For example, coffee, which has an easily distinguishable and unmistakable odor, consists of 108 furans, 79 pyrazines, 74 pyrroles, 70 ketones, 44 phenols, 31 hydrocarbons, 30 esters, 28 aldehydes, 28 oxazoles, 27 thiazoles, 26 thiophenes, 21 amines, 20 acids, 19 alcohols, 13 pyridines and 13 thiols/sulfides (Hodgins and Simmonds, 1995). Actual odor perception is the result of mutual interactions (additive, synergistic, antagonistic or compensative) of all these compounds. Odor molecules are generally small and polar which can be detected by humans at levels below 1 ppb (Bartlett et al., 1997).

The mammalian olfactory system can discriminate aromas without separating mixtures into individual compounds. Signals sent from receptor cells in the olfactory system seem to be decoded by the brain using a kind of pattern recognition (Moulton, 1963). Analysis techniques can objectively discriminate odors, but the sample must be separated into its individual components. Thus, there is a significant interest in the development of sensor arrays to mimic the human olfactory system for detection of odors.

4.3.1. Definition

Pattern recognition to detect and possibly identify the type of odor molecule and/or odor compounds using an integrated sensor system has been reported. (Oishi et al., 1988; Aishima, 1991; Hodgins and Simmonds, 1995; Hivert et al., 1995). Based on an analogy of the olfactory mechanisms of living organisms, several types of sensor systems have been developed. Current electronic nose (e-nose) technology may be more appropriately defined as odor sensors, aroma sensors, gas sensors and flavor sensors since there are no strong link with the human olfactory system (Mielle, 1996).

The term "electronic nose" or electronic olfactory sensing system is applied to an instrument which is comprised of an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognizing a simple or complex odor profile without it being separated into its individual components (Gardner and Barlett, 1994). Complex mixtures of compounds may be detected as a unitary stimulus without separation into their components, while retaining the ability to discriminate small changes in the components or concentrations of the components in such mixtures. This processing occurs in fractions of a second (Persaud and Pelosi, 1985).

4.3.2. Principles

The basic electronic nose system includes a method to generate headspace over the sample being tested, presentation of the headspace gas to the sensors, and a computer to record the sensor's response and to analyze the data (Culter, 1997). Figure 9 presents the principle of the e-nose system compared to the human nose. The electronic nose system parallels the human olfactory system in the following ways. Each chemical sensor represents a group of olfactory receptors and produces a time-dependent electrical signal with response to an odor. In addition, the human olfactory system classifies and memorizes odor responses in the cerebral cortex of the brain which is equivalent to the use of pattern recognition software in the electronic nose (Bartlett et al., 1997).

4.3.3. Sensor technology

Several types of sensors are commercially available. These include metal oxide sensors, bulk or surface acoustic wave devices and conducting polymer sensors. Each sensor has its own functional mode and offers different characteristics in terms of selectivity and sensitivity to different compounds. Figure 10 presents the schematic diagram of a metal oxide sensor, bulk and surface acoustic wave device and conducting polymer sensor.

Metal oxide sensors

These sensors consist of an electrically heated ceramic coated with a semi-conducting film i.e. tin or zinc oxide. This film can be doped with various precious catalytic metals to shift the selectivity spectrum towards different chemical compounds. A sensor adsorbs oxygen from the air into lattice vacancies (Figure 10a). Oxygen can trap free electrons from the conduction band of the semiconductor, thus increasing the electrical conductance. This

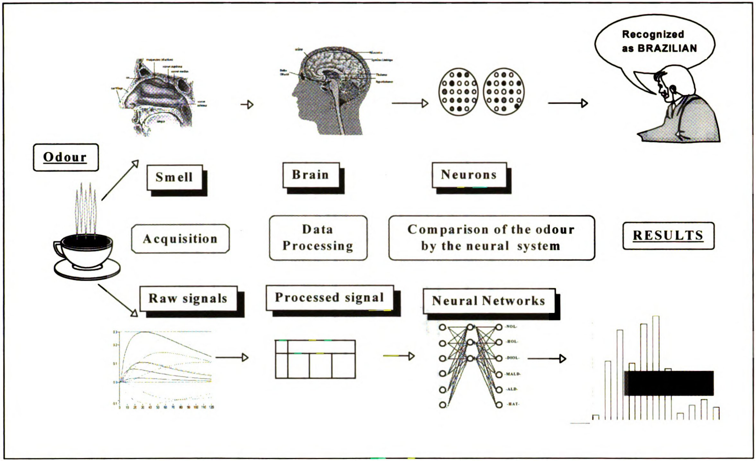
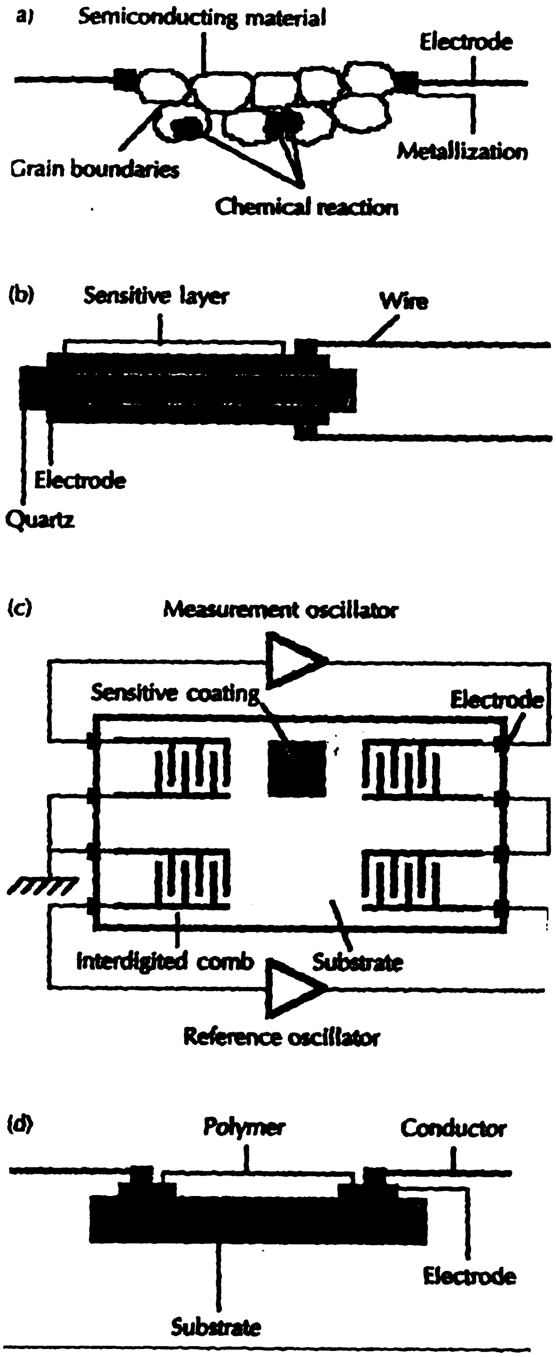


Figure 9 Principle of the electronic nose system

(**Source:** Alpha M.O. S. America, Hillborough, NJ)



a) Semi-conducting metal oxide sensor
b) Piezoelectric bulk acoustic wave (BAW) sensor
c) Piezoelectric surface acoustic wave (SAW) sensor
d) Conducting polymer sensor

Figure 10 Schematic diagram of sensors used in the e-nose system (Mielle, 1996) response decreases in the presence of a reducing gas that reacts with adsorbed oxygen; thus, the temporary and reversible adsorption of volatile reducing compounds at the surface decreases the electrical resistance (Mielle, 1996).

The sensitivity of metal oxide sensors is quite good. They are relatively resistant to humidity and to aging. However, they have slow baseline recovery, especially when reacting with high molecular weight compounds, and can be poisoned in reaction with sulfur compounds and weak acids. This sensor operates at high temperature (250-600°C) to avoid interference from water and to provide rapid response and recovery time. Table 4 presents examples of metal oxide sensors commercially used in the Fox e-nose system (Alpha M.O.S. America, Hillsborough, NJ). Several types of metal oxide sensors are available for specific applications.

Piezoelectric crystals (Bulk acoustic wave sensors; BAW sensors or quartz resonators)

Quartz resonator odor sensors consist of a piezoelectric quartz crystal oscillator coated with a sensing membrane, which must be chemically and thermally stable, such as acetyl cellulose or lecithin. The adsorption of odor molecules onto the membrane results in a decrease in the resonant frequency due to an increase in mass. The sensitivity depends on the operating frequency and the selectivity depends on numerous factors that can be more difficult to control such as the temperature and humidity of the carrier gas.

Table 4 Examples of metal oxide sensors used in the Fox e-nose system

Description		Application	Metal oxide sensor			
			P Type	T Type	SX Type	SY Type
Non polar volatile	Hydrocarbons Methane and propane	Cooking, roasting of coffee, petrochemical	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 and aromatic compounds (Toluene, Xylene etc.)	Paint &polymers industry (PE, PP)	P70/0 P70/1	T70/0-70/1 T70/2-70/3	SX23	SY/GC
		Smoke detection Hydrogen bonding	PA3	TA3		
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 and 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 food stuffs	Environment and applications in smoke detection	PA3	TA1 TA3	SX00 SX80 SX84	

Nakomoto et al. (1993) successfully identified perfumes and flavors by using quartz resonators with a system of eight different types of resonator membranes, initially designed to inspect whisky aroma. Five different perfume types were clearly separated using principal components analysis. The same experiment carried out using semiconductor gas sensors showed no separation. The authors, therefore, concluded that the quartz resonator sensors were far superior to semiconductor gas sensors.

Surface acoustic wave (SAW) sensors

The operating principles of SAW and BAW sensors are similar. The radio frequency oscillations are transmitted by the electrical field created by electrodes deposited at the surface of the solid. This sensor is less likely to suffer from sensor drift. However, both BAW and SAW sensors have difficulty due to batch-to-batch manufacturing differences and a drift in the response when the temperature changes.

Conducting polymer sensors

Conducting polymer sensors are obtained by electropolymerization of a thin film of polymer across the gap between gold-plated electrodes (Figure 10d). The electrical conductance of this film changes according to the odor molecules adsorbed onto its surface. Two polymers often used are polypyrroles and polyanilines. Conducting polymer sensors can operate at room temperature. However, their drawbacks include long response time, inherent drift over time or with change of temperature, high cost and poor batch-to batch reproducibility.

4.3.4. Data interpretation

Pattern recognition techniques based on multivariate analysis have become an effective tool to process the multidimensional data obtained from GC and GC-MS analysis. In addition to food flavor research, multivariate techniques are successfully applied to gain better understanding of data obtained from the electronic nose. Commercial electronic nose systems often come with either multivariate analysis or neural network software.

Multiple regression analysis and its derivatives, including partial least squares regression (PLS), has been frequently used for correlating instrumental data to sensory properties. Factor analysis and principal components analysis (PCA) are widely used for searching latent factors and extracting information as unsupervised pattern recognition.

When PCA is applied to a data set, the original variables are mathematically converted into a set of new variables or so called components, where each component is expressed as a linear combination of the original variables. The coefficients for the ith component ($a_{1i}, a_{2i}, a_{3i}, \ldots, a_{mi}$) are determined by the standard matrix operation of transforming the covariance or correlation matrix into a diagonal matrix with diagonal elements ($\lambda_1, \lambda_2, \lambda_3 \ldots \lambda_m$). The λs, called the eigenvalues, represent the variances of the components. The importance of each component is determined by its variance percentage, 100 x ($\lambda i / \Sigma m \ \lambda j$). The first few components, called the principal components (PCs), have the largest value of λ and, therefore, contain the maximum amount of information. The remaining components, with decreasing values of λ, contain progressively less meaningful information and more random noise.

In most PCA applications, the samples and the original variables are projected onto the first two principal components using two arbitrary scales. Two plots are commonly displayed: score and loading plots. Score plots show the positions of samples in the plane constructed by the two components. The loading plot reveals the contributions from each of the original variables to the principal components (Chien and Peppard, 1993).

A model based on a partial least squares (PLS) technique may be used to predict individual scores from instrumental data. PLS is based on a regression technique. The model is normally developed using a 'training' set of data. Y is the matrix containing quantitative measures, whereas Y' is the matrix containing the predictive values and X is the matrix built with detector measurements (i.e. metal oxide sensor). The PLS model looks for a B matrix that minimizes the distance between Y and Y' with $Y' = X B$.

Li and Kwok (2000) applied PCA and PLS to solve the problem of sheetbreaks during a pulp and paper making process. The PLS model was established to take into account all factors involved in the process. The effectiveness of the approach was investigated using data collected from pulp and paper machines.

Forsgren and Sjostrom (1997) identified carton board qualities using gas chromatography or gas sensitive sensors in combination with multivariate data analysis. 40 different board samples were collected containing a total of 8167 detector responses. Applying multivariate analysis to the GC data, the first principal component differentiated board containing recycled fiber from virgin fiber. The second PC was strongly influenced by peaks representing volatile compounds from the coating, and the third component was influenced by the type of pulp used as raw material.

Tang et al. (1999) correlated the instrumental results with the sensory data of wheat noodles using multivariate techniques. For instrumental sensory relationships, PCA, PLS and procrusters analysis (PA) confirmed that the instrumental and sensory analysis procedures reached a true consensus.

4.3.5. Applications

The electronic nose systems can be used for a wide variety of applications, such as in the food and beverage industry, for flavor and fragrances, petrochemicals, pharmaceuticals and heath care, as well as in the packaging industry (Oishi et al., 1988; Pitt, 1996; Hodgins and Simmonds, 1995; Mielle, 1996; Bartlett et al., 1997). The electronic nose systems can be used for routine quality control, in comparing new developmental products, and investigation of taints and evaluation for counterfeit products (Pitt, 1996; Hodgins and Simmonds, 1995).

In the food and beverage industry, Funazaki et al. (1995) investigated the possibility of monitoring the quality of meat freshness using a single semiconductor gas sensor. Ethyl acetate is formed as a result of bacterial putrefaction of meat, and the sensor was shown to have excellent sensitivity to ethyl acetate, over the 10-200 ppm range at 300°C. The use of a gas sensor also correlated well with the traditional assessment method.

Aishima (1991) showed that a semiconductor gas sensor array, in conjunction with pattern recognition techniques such as discriminant analysis and cluster analysis, could discriminate between two ground coffees, *Coffea arabica* and *Coffea robusta* against freeze-dried and spray-dried commercial instant coffees. Tan et al. (1995) used a set of six sensors to identify three different types of colas and six different brands of sausage. In addition, an array of 20 conducting polymer sensors was used to discriminate a slight difference between samples of English Cheddar cheese: mild, medium and mature (Persaud and Travers,1997).

Persaud and Travers (1997) used an array of 20 conducting polymer sensors to test several flavor compounds: citral (lemon), citronellol (rose), cinoel (eucalyptus) and isoamyl acetate (banana). The neural network had a 95% success rate in recognizing the pattern presented. Hodgins (1995) evaluated a number of different fragrances using an e-nose with six sensors. The results show quite clearly that differences can be detected in fragrances. Moreover, the instrument clearly discriminated between the satisfactory and unsatisfactory product of two fruity fragrances.

Other potential applications of using the electronic nose system are found in agricultural, food safety and medical diagnostics. Warburton (1996) reported on the use of an electronic nose system in a fruit-breeding program at the Scottish Crop Research Institute (SCRI). The results showed that there was a very strong relationship between the aromas detected by the electronic nose and human sensory perception of fruit flavor.

4.3.6. Applications of an electronic nose system in the packaging industry and water analysis

Forsgren and Sjostrom (1997) identified 40 different food packaging paperboard and paper samples using gas chromatography and gas sensitive sensors in combination with multivariate data analysis. The results from the GC analysis showed that the first principal component separated samples containing recycled fiber from samples containing only virgin fiber. The e-nose was capable of discriminating between paper samples obtained from different paper mills. Thus, the investigators concluded that the two analytical techniques had a capability to recognize 'fingerprints" of board and paper which could be further developed to partly replace human sensory panels.

The use of an electronic nose system for analysis of paperboard is reported by Culter (1997). The author showed that paper mills produced board of different volatile composition, since each mill used a different recipe and slightly different papermaking chemicals for preparing fiber. In addition, an electronic nose system with discrimination analysis has proven successful for monitoring the lamination process. Laminated films produced at a fast press speed had an unacceptable odor level.

Correlation between human sensory and electronic sensors for odor analysis of paperboard using multivariate techniques was also studied by Willing et al. (1997). Using Partial Least Squares (PLS) regressions, the responses from some electronic sensors correlated well with a selected number of panel descriptors, though some sensors did not fit with the descriptors.

Stuetz et al. (1998) used an electronic nose system with 12 polypyrrole conducting polymer sensors to detect taint compounds in raw and treated potable water. Raw and treated water samples were tainted with geosmin, methylisoborneol, 2-chlorophenol, phenol diesel and 2-chloro-6-methylphenol at various concentrations. Using multiple discriminant analysis, no overlapping occurred between any of the tainted and untainted samples. Close grouping between repeated tests also indicated that the sensor responses were reproducible.

4.3.7. Limitations

A sensor array used for discrimination between odors was first demonstrated by Persaud and Dodd in 1982 (Hodgins and Simmonds, 1995). Currently, research on sensor technology has focused on high selectivity and sensitivity, as well as robustness of the sensors. In addition, data analysis techniques using either chemometric or neural networks to interpret the data (easy understanding and long-term reference) are still under development.

A disadvantage of the electronic nose is that it cannot be used to identify and characterize a single odorant or to make subtle distinctions between different odors. One approach to solve this problem is to use high resolution gas chromatography/selective odorant measurement with multi-sensor array

(HRGC/SOMSA). In this method, different types of sensors are used along with a Flame Ionization Detector (FID). It is possible to select suitable sensors for the detection of odor active compounds, which have a higher sensitivity to some odor-active compounds than the FID. However, it is still difficult to exclude the influence of the remaining vapors, which are not related to the flavor of the foodstuff (Bucking et al., 2000).

In addition, the electronic nose system is subject to both sensor drift and system drift. Sensor drift occurs due to the aging or degradation of individual sensors, while system drift encompasses all sensors. Drift results in gradual change of output over time without change in input. Thus, it leads to a major problem with the reproducibility of the system. It is hard to get consistent responses if the sensors age over time or can be poisoned by specific chemicals. Calibration can be performed to compensate for sensor drift, as can use of a formal neural network. Replacing sensors can help to solve the problem; however, batch-to-batch variability in manufacture of individual sensors can result in variability in sensor selectivity. Typically, sensor lifetime varies from several months to 1-2 years (Zubritsky, 2000).

The sensors used in the e-nose system are also sensitive to moisture. Conducting polymer sensors are more sensitive to humidity than metal oxide sensors. Using a filter and an air conditioning unit to remove excess humidity from the carrier gas can minimize this problem (Mielle, 1996; Culter, 1997).

Performance of sensors used in the electronic nose system was evaluated by Schaller et al. (1999). The investigators used metal oxide sensors (MOS), conducting polymer sensors, quartz microbalance sensors, and metal oxide semiconductor field effect transistor sensors as well as mass spectrometry to follow the ripening of Swiss cheese. The results showed that metal oxide sensors gave the best discrimination. However, they seemed to be damaged by short-chain fatty acids in the Swiss Emmental cheese. Conducting polymer sensors showed poor sensitivity to volatile compounds of cheese due to rapid sensor drift. The response of quartz microbalance sensors was too weak to detect differences between cheese samples. Discrimination using a newly designed mass spectrometry system was difficult due to the low sensitivity of the instrument to the volatile compounds of cheese. Metal oxide semiconductor field effect transistor sensors did not give good discrimination between the samples.

Aparicio et al. (2000) used a sensor array of 32 conducting polymers to detect the rancid flavor in virgin olive oils. There may have been sensor saturation in some sensors due to the great number of chemical compounds in the rancid olive oil. Hivert et al. (1995) monitored complex food flavor mixtures containing flavors such as hexanal and 1-hepten-2-one using a tin oxide sensor array in conjunction with gas chromatography. However, calibration of the system using flavor mixtures was a problem.

5. Surface analysis techniques for packaging applications

Surface analysis techniques such as Infrared Spectroscopy and Electron Spectroscopy for Chemical Analysis (ESCA) have proven to be useful in packaging applications. Surface analysis techniques can be used for failure analysis, product development, quality control and ensuring adherence to regulatory requirements.

5.1. Fourier Transform-Infrared (FT-IR) Spectroscopy

FT-IR spectroscopy has proven to be very useful in the packaging industry for its qualitative analysis ability, especially in polymer identification. FT-IR can be used in either transmission or reflection modes for quantitative analysis.

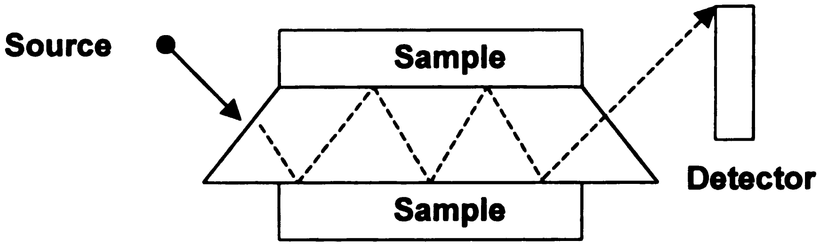


Figure 11 Attenuated Total Reflectance (ATR) technique

Fourier Transform-Infrared (FT-IR) spectroscopy with Attenuated Total Reflectance (ATR) provides accurate quantitative analysis of surfaces from 0-2.5 μm (Urban, 1998). Paralusz (1974) used ATR to investigate and characterize the functional layers of an adhesive tape. ATR was used for quality identification of tape components and interpretation of internal reflection spectra of elastomer blend component tape. The investigator concluded that the attenuated total reflectance techniques applied to tapes might be useful in the analysis of similar types of polymers and polymer blends.

Fischer and Eysel (1994) used both FT-IR transmission and ATR methods to study polyethylene surface sulfonation. In addition, structural and quantification analysis of surface modified polyvinylidene fluoride films using ATR FT-IR spectroscopy was illustrated by Kuhn et al. (1987). Mizoguchi et al. (2000) used FT-IR analysis to study the cross-linking of vinyl ester resin during the curing process.

Kuijk et al. (1992) and Van Leeuwen et al. (1997) used FT-IR transmission mode spectroscopy to determine the oxidation index of a PE film surface. The oxidation index was calculated based on the ratio between absorption values at 1720cm^{-1}and 2660cm^{-1}, which are the nominal regions for carbonyl and allyl groups, respectively. The higher the number of carbonyl groups on the surface, the higher the absorption in this region, and thus the higher oxidation level.

5.2. Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA is an instrumental in-situ surface analytical technique that has been developed over the past 20 years. The technique was originally called x-ray photoelectron spectroscopy (XPS),and the terms 'electron spectroscopy for chemical analysis' (ESCA) and 'XPS' are interchangeable. ESCA is the surface analysis technique used to analyze the outermost atomic layers of a material with very high elemental and molecular sensitivity. It can provide extensive chemical information, including classification of organic materials and contamination (Singer, 1988; West, 1996).

In ESCA, electrons in a sample absorb energy from incident X-rays, and photo emission then occurs. These photoelectrons are emitted with kinetic energies related to their atomic binding energies (Brigg, 1996). The kinetic energy spectrum of core electrons that are ejected from surface atoms is recorded. Electrons are ejected following irradiation of the sample by soft X-rays. The energy of the emitted electrons is such that only electrons from atoms in the outermost surface region (3-5 nm) can escape from the sample for detection. Thus, both elemental composition and chemical bonding information can be obtained. Surface elemental compositions can be determined by ESCA from the peak intensity detected for any element with atoms heavier than helium. Similarly, information on oxidation states and functional groups can be measured accurately (West, 1996).

ESCA is popular for polymer surface analysis because it provides the elemental composition without major quantification problems, and structural information, does not suffer unduly from sample charging or radiation effects, and sample shape is not restricted (Brigg, 1996; West, 1996). Thus, this technique can be used to determine chemical composition and chemical and molecular state information from surfaces and interfaces.

West (1996) illustrated several applications for ESCA in pharmaceutical packaging. These included defect and failure analysis, adhesion failure or degradation of adhesive bond, and migration of polymer additives. The problem of adhesion failure of metallized paper labels (beer and beverage industry) was also identified by ESCA (Modhajny, 2000). Moreover, ESCA can help to identify the optimum level of surface treatment required for specific applications, such as coating and preventing of adhesion failure.

Fay (1993) reported that in addition to Scanning Electron Microscopy (SEM), ESCA measurement was used to investigate the aluminium oxide layers on the surface of the aluminium coating and aluminium interface with PP during metallized film production. Cheatham et al. (1993) used ESCA for surface characterization of an LDPE extrusion coating after flame and corona treatment. The effect of corona treatment on printability of polyolefin film was studied by Kulsetthanchalee (1998). ESCA was performed to characterize the surface composition of film samples. The authors concluded that the higher the corona treatment, the higher the surface free energy values, as well as better adhesion of the ink to the film.

Van Leeuwen et al. (1997) determined the oxidation index after fabrication of LDPE cast film with and without vitamin E after fabrication using FT-IR transmission mode spectrophotometry. The oxidation index was calculated based on the ratio between absorption values at $1720\text{cm}^{-1}$and 2660cm^{-1}. In addition, the authors used ESCA to obtain more information on the surface oxidation of LDPE during storage. The authors found that the atomic oxygen level on the surface of LDPE film without vitamin E increased greatly after 12 weeks storage due to migration of volatile degradation products from the LDPE bulk to the film surface. The results also agreed with the results from GC-MS analysis.

CHAPTER II

MATERIALS AND METHODS

This research was designed to evaluate the ability of the electronic nose system to detect off odors, compared to more traditional detection techniques such as GC-MS and sensory analysis. The electronic nose system was used to investigate off-odors from one gallon commercial HDPE water bottles. The containers were fabricated using two types of antioxidants, and two processing conditions. After processing, HDPE container samples were subjected to electronic nose and GC-MS analysis. The containers were then filled with 1.5 L high purity water and stored at 38 ± 2°C for 6 months. Water samples from the respective containers were sampled and evaluated for off-odor using the electronic nose, GC-MS and sensory analysis at three-month intervals. In addition, surface analysis was performed on HDPE containers using FT-IR spectrophotometry, and ESCA measurement, prior to, and after three and six months storage. The experimental design is summarized in Figure 12.

Experimental Summary

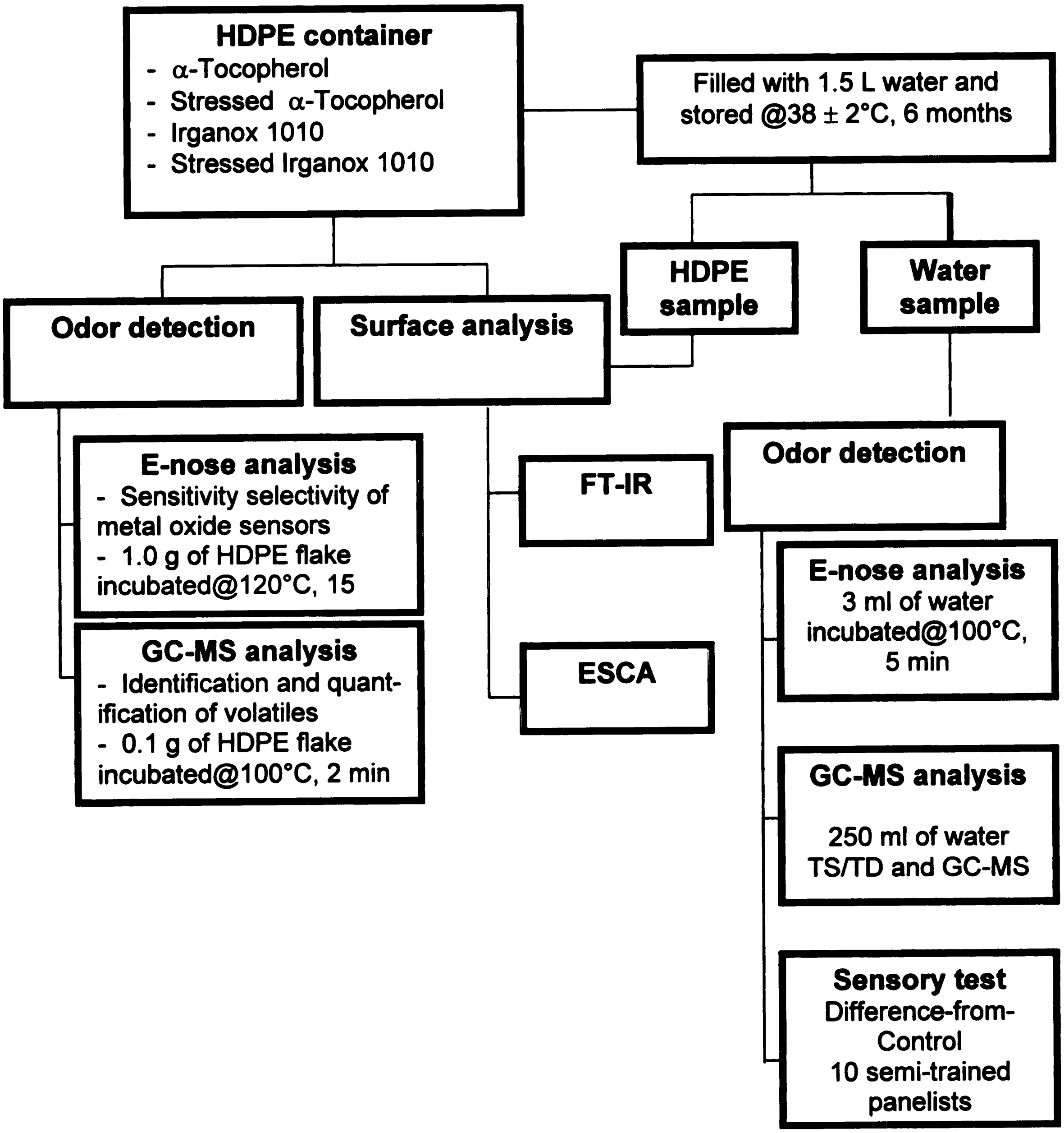


Figure 12 Methodology for volatile and surface analysis from HDPE containers

1. Analysis of the off-odor released from HDPE containers using the electronic nose system and GC-MS analysis

1.1. Sensitivity and selectivity of the metal oxide sensors used in the electronic nose system

1.1.1. Electronic nose system

The Fox 3000 electronic nose system (Alpha M.O.S. America, Hillsborough, NJ) used in this study consisted of 12 metal oxide sensors with partial specific response to specific volatile compounds. Sensor names were 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

The electronic nose system was equipped with an air conditioning unit (ACU 500, Alpha M.O.S America, Hillsborough, NJ), which helped to control temperature and humidity of the carrier gas. The system was connected to an auto-sampler (HS 100, Alpha M.O.S America, Hillsborough, NJ), and the samples injected into the system automatically. During testing, the samples (i.e. HDPE flakes, water samples) were put into 10 ml vials and sealed with Teflon septum caps (Alpha M.O.S. America, Hillsborough, NJ). The Fox software version 6.0 (Alpha M.O.S America, Hillsborough, NJ) was installed for data interpretation.

1.1.2. Chemical standard

In order to determine the detection threshold of nonanal (Nonyl aldehyde; Aldrich® Chemical Co. Inc., Milwaukee, WI), with respect to the twelve metal oxide sensors, pure nonanal was diluted in triacetin (1,2,3-Triacetylglycerol; Sigma® Chemical Co., St. Louise, MO). Properties of the nonanal and triacetin used in this study are shown in Appendix A:

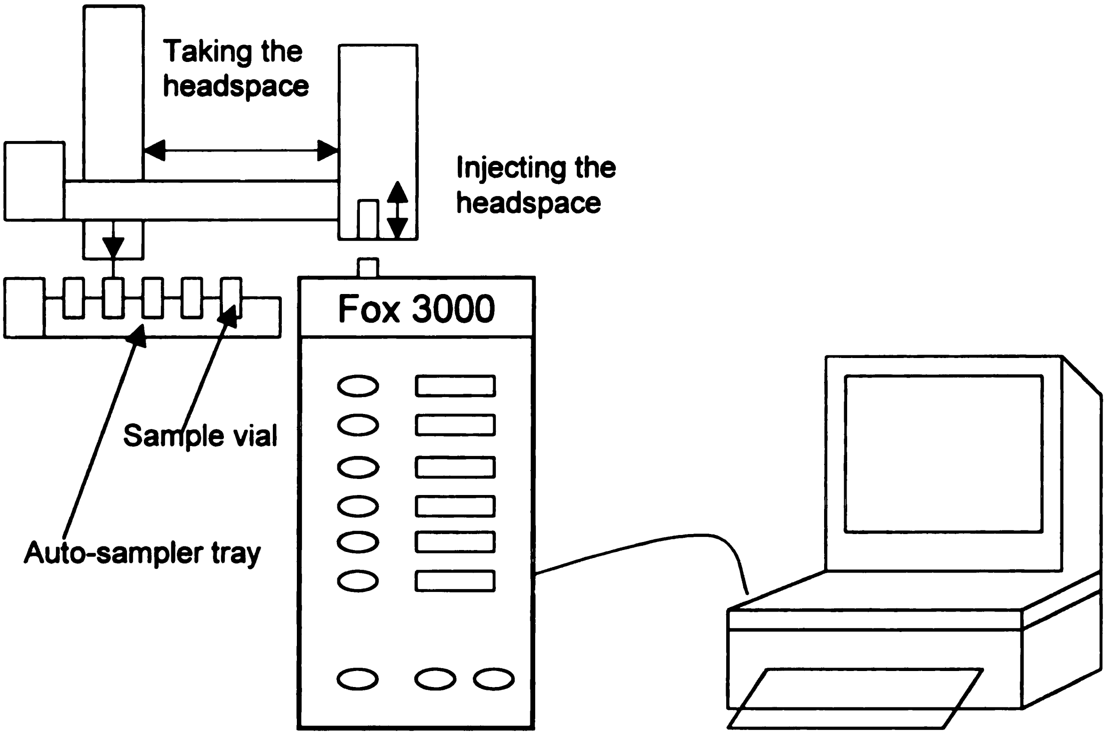


Figure 13 Schematic diagram of the Alpha M.O.S. Fox electronic nose system

Triacetin was used as a dilution solvent to minimize the effect of sensor response interference since all sensors barely respond to triacetin. Nonanal is a volatile compound and can be found in HDPE (containers), and is able to cause off-odor even when present in a small amount (Ho et al., 1996; Kosznowski and

Piringer, 1986). The study focused on nonanal as the dominant off-odor compound due to its low odor threshold.

1.1.3. Determination of sensitivity and selectivity

A dilution series of 0.01 to 100 ppm (volume/volume) and 0.1 to 10% (volume/volume) of nonanal in triacetin was prepared. A specific volume (1.0 ml) of the pure and diluted nonanal in triacetin was transferred to an auto-sampler vial and the vial was capped before placing it into an auto-sampler tray. The vial was then transferred to the agitator in order to generate headspace volatiles from the sample. Samples were tested in triplicate (at least) for each dilution.

Compressed air at a flow rate of 300 ml/min flowed to the sensor array in the Fox 3000 unit. A specific volume (5.0 ml) of the sample headspace was injected into the carrier stream. The headspace sample was then passed over the sensors, for a total analysis time of 40 min. The operating conditions [3]were; acquisition time = 600 sec; injection volume = 5000 μl; injection speed = 2500 μl/min and fill speed = 2500 μl/min.

Since all data involved several sensor responses, time slices and sample replication, multivariate techniques such as Principal Components Analysis (PCA), and Discriminant Function Analysis (DFA) were used to increase understanding of the data obtained from the electronic nose system.

Principal Components Analysis (PCA) reduces the number of variables

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[3] The testing conditions were optimized based on the testing conditions for the HDPE samples.

represented by the sensor responses and transforms the multiple dimensional data into common vectors. The database is created as a new set of metrics of *m* variables and *n* objects. The variables are the sensors; and the objects are combinations of the original variables. Data presentation can be performed on a two or three dimensional space based on selected components. PCA is a useful tool to assess the similarity or dissimilarity between the samples as well as to provide more information about the relationships between variables (sensors).

The Partial Least Squares (PLS) Technique is based on linear regression analysis, which helps to predict and enhance the capability of the Fox 3000 electronic nose system, in terms of quantitative analysis. PLS is performed to determine the sensitivity of the system to a specific volatile compound. Based on linear regression, the Partial Least Squares (PLS) technique is designed to build a model that is able to predict quantitative information, i.e. sensory scores, and concentration of a specific volatile compound for each sample analyzed. Original data is transformed into a new linear vector and a plot of the actual values versus the predicted values can be illustrated based on input quantitative information. Thus, the unknown concentration or sensory score can be predicted.

Principal Components Analysis (PCA) and the Partial Least Squares (PLS) technique were used to discriminate and evaluate the correlation between each dilution. Good discrimination was obtained by PCA, which gave an indication of the significant difference between closed dilutions. Additionally, a high correlation was provided by PLS, which showed the performance of the system in predicting the unknown values. Thus, the selectivity and sensitivity of the metal oxide sensors used in the electronic nose system were justified and used in this study.

1.2. Analysis of the off-odors released from fabricated HDPE containers using the Fox 3000 electronic nose system

1.2.1. Sample preparation

One gallon HDPE water containers (Figure 14) were fabricated by Chevron Phillips Chemical Co., LP (Orange, TX) using two antioxidants: α-Tocopherol and Irganox 1010 (Giba Specialty Chemicals Inc.), under normal and abusive processing temperature conditions. Processing temperatures at the feed zone, transferring zone and metering zone respectively were 143-149°C (290-300°F), 168°C (335°F) and 174°C (345°F) for normal conditions, and 177°C (350°F), 191°C (375°F) and 204°C (400°F), for abusive conditions. 500 ppm of α-Tocopherol was incorporated into samples of the HDPE resin, while 250 ppm of Irganox 1010 was used to fabricate other HDPE container samples.

Sample codes were assigned as follows:

B: α-Tocopherol sample, or HDPE containers with α-Tocopherol as antioxidant, processed at normal temperature conditions.

F: Stressed α-Tocopherol sample, or HDPE containers with α-Tocopherol as antioxidant, processed at abusive temperature conditions.

E: Irganox 1010 sample, or HDPE containers with Irganox 1010 as antioxidant, processed at normal temperature conditions.

D: Stressed Irganox 1010 sample, or HDPE containers with Irganox 1010 as antioxidant, processed at abusive temperature conditions.

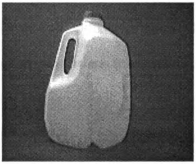


Figure 14 HDPE container used in this study

1.2.2. Analysis of the off-odors from HDPE containers

Samples of the HDPE container wall were cut into small flakes. The samples were taken from the side panels at the same location from six container samples. Approximately one gram of the sample was added to an auto-sampler vial. The vial was placed in an auto-sampler before being transferred to the agitator and incubated at 120°C for 15 min to generate headspace volatiles from the HDPE sample. The volatiles generated were then conveyed directly to the sensor array. The sensor response intensity was recorded as a function of time. Stabilization of the sensors was required between each measurement, so there was no effect of carry over from the previous run.

Preliminary studies established the optimum conditions for volatile generation from HDPE, and included a one gram sample incubated at 120°C for 15 minutes. Each container sample was tested in triplicate for each trial and six trials were conducted on non-consecutive days to confirm the system repeatability.

Multivariate statistical analysis such as Principal Components Analysis (PCA) was conducted to differentiate between the HDPE samples. In addition, group distance was calculated to determine the sample similarity.

1.3. GC-MS analysis of the off-odors released from HDPE containers

1.3.1. Identification of specific volatile organic compounds associated with off-odor from HDPE containers

A sample of the HDPE container wall was cut into small flakes. The sample was taken from the same side panel of the same container used for the electronic nose analysis. Approximately 0.1 gram of sample was added to a 0.5 ml vial. The vial was placed in the thermal desorption unit (Thermex; LECO® Co., St. Joseph, MI) and incubated at 100°C for 2 min to generate headspace volatiles. The volatiles generated were then conveyed directly to the GC-MS system, which was equipped with a 1 m (length) x 0.25 mm (internal diameter) intermediate polarity fused silica capillary column (Supelco Inc., Bellefonte, PA). The volatile compounds were collected at (-20)°C, for 5 min before GC analysis. Triplicate samples of each container sample were analyzed.

A spitless injector at 250°C was used to introduce the volatile compounds onto a fused silica capillary column. The capillary column used was SPB-5, with dimensions as follows: 30 m (length) x 0.32 mm (internal diameter) and 1 μm film thickness (Supelco Inc., Bellefonte, PA). The initial column temperature was

40°C, and was then increased at a rate of 50°C/min to 100 °C and 30°C/min to 250°C where it was held for 7 min. The initial pressure was 15 psi. One minute after injection the pressure was increased at a rate of 1.0 psi/min to 20 psi and was held for 5 minutes. Helium was used as a carrier gas(5 ml/min flow rate). The operating parameters of the mass spectrometer were: ion source temperature = 200°C; transfer line temperature = 225°C; detector voltage = 1580 volts; scan range, m/z = 33-350; acquisition rate = 40 spectra/sec; solvent delay 25 sec and total time = 460 sec.

Identification of the volatile compounds was determined by comparing their mass spectra to the standard library spectra. In addition, authentic standards of selected compounds, such as nonanal, hexane, dodecane, etc., were also analyzed under the same test conditions in order to obtain the correct retention time and to confirm their identifications. The Time-of-Flight mass spectrometer (LECO®PEGASUS®II; LECO Co., St. Joseph, MI) was interfaced to a gas chromatograph Model 6890 (Hewlett Packard Co., Chicago, IL), and was used for the above analysis.

1.3.2. Quantification of specific off-odor compounds from HDPE containers

The ThermEx/Time-of-Flight PEGASUSII mass spectrometer interfaced to a gas chromatograph Model 6890 (Hewlett Packard Co., Chicago, IL) was used to identify the volatile off-odor compounds from the respective HDPE samples as described above. Identification of selected volatile compounds was determined by comparing their mass spectra to standard library spectra. Quantitative measurement of individual components, such as nonanal, was obtained by peak area comparisons to an external standard of the specific compound analyzed. The amount of nonanal in the volatile headspace from the HDPE container sample was estimated using a calibration curve (0.1 g of HDPE sample, heated to 100°C, so a sample of released volatiles could be detected by GC-MS analysis, as described above).

A dilution series of 10-500 ppm (volume/volume) of nonanal in squalane (2, 6, 10, 15, 19, 23-hexamethyltetracosane; Sigma® Chemical Co., St. Louise, MO) was prepared. Squalane is a high molecular weight compound (Appendix A) which makes it less volatile at room temperature. Because of its low volatility, squalane was used to dilute nonanal to hold the sample, thus, avoiding loss following injection. A small amount of glass wool was placed into a vial, and 0.5 μl of nonanal was injected into the vial with a 1 μl syringe (Hamilton Co., Reno, NV). The vial was then placed in the thermal desorption unit (Thermex; LECO® Co., St. Joseph, MI) unit and incubated at 100°C for 2 min to generate the headspace volatiles. The volatiles in the headspace were then directly transferred to the GC-MS system. Each dilution was evaluated using the same conditions. All volatiles were assumed to be completely transferred to the GC-MS system since there was no trace of nonanal was found during the next run. Triplicate samples (or more) were evaluated for each dilution. The Time-of-Flight mass spectrometer (LECO®PEGASUS®II; LECO Co., St. Joseph, MI), interfaced to a gas chromatograph Model 6890 (Hewlett Packard Co., Chicago, IL) was also used for the above analysis.

2. Evaluation of the off-odor compounds released from HDPE containers using instrumental analysis and sensory evaluation

2.1. Sample preparation

The four HDPE container samples were filled with 1.5 L high purity drinking water. Deionized water was obtained from the Food Science Department (Michigan State University, East Lansing, MI). It was then further treated by passing it through a commercialized pitcher filter (Brita®; Brita Products Co., Broadway, CA), which can remove 93% of any lead and copper, as well as reducing chlorine. The water was stored in glass containers prior to filling into experimental HDPE containers. The containers were stored at 38 ± 2°C and 65 ± 5% RH for six months in a controlled environmental chamber, with sampling and analysis every 90 days.

Water samples were then served to panelists and sensory evaluation was conducted. Additional samples were simultaneously analyzed for organic volatile compounds that had transferred into the water sample from the package, using a thermal stripper, thermal desorption GC-MS analysis procedure, as well as the electronic nose system. Water packaged in a glass container and stored under identical conditions was used as the reference sample. Water samples, which were filled into the containers and equilibrated for 24 hours at ambient temperature, were also subjected to sensory evaluation (initial control treatment).

2.2. Odor analysis of water samples using the Fox 3000 electronic nose system

A specific volume (3 ml) of each water sample was transferred to an auto-sampler vial and the vial was capped before placing it into an auto-sampler tray. The vial was then transferred to the agitator in order to generate headspace volatiles from each sample.

Compressed air at a flow rate of 300 ml/min flowed to the sensor arrays in the Fox 3000 unit. A specific volume (5.0 ml) of the sample headspace was injected into the carrier stream. The headspace sample was then passed over the sensors, for a total analysis time of 25 min. The following operating conditions were used: air flow rate = 300 ml/min; incubation temperature = 100°C, incubation time = 5 min; acquisition time = 250 sec; injection volume = 5000 μl; injection speed = 2500 μl/min; fill speed = 2500 μl/min. 5 psi of compressed air was used as the carrier gas.

Principal Components Analysis (PCA) was performed to discriminate between the four water samples from the four HDPE containers and the water sample from the glass container.

2.3. Identification and quantification of specific off-odor compounds in water samples using GC-MS analysis

A thermal stripper with thermal desorption system, coupled to a GC-MS system was employed to identify volatile compounds migrating into the water samples. GC-MS analysis was performed using a capillary gas chromatograph

Model 5890 (Hewlett Packard Co., Chicago, IL) directly interfaced to a high-resolution quadruple mass spectrometer (HP 5970) equipped with a mass selective detector, and a Chemstation data system (HP 300).

A thermal stripper technique was used to prepare each sample by collecting volatile compounds onto an absorbent trap (Figure 15). A preliminary study was conducted to obtain the optimum conditions for the analysis of sorbed off-odor volatile compounds in the water samples. 250 ml of the water sample was transferred into the vial and placed into the Dynamic thermal stripper model 1000 (Dynatherm Analytical Instruments, Inc., Kelton, PA). Each sample was preheated at 100°C for 15 min before helium (99% purity, BOC Gases, Murray Hill, NJ) was used to purge and carry the volatile compounds through the absorbent tube. A purge time of 10 min at 100°C at 100 ml/ min flow of helium gas was used. The sample was then dried at 75°C for 9 min under 50 ml/min flow of helium gas. The volatile compounds in the aqueous phase were collected using the prepacked adsorbent tube. Samples were prepared and analyzed in triplicate.

Prepacked adsorbent tubes (Carbotrap™ 400) were obtained from Supelco Inc. (Bellefonte, PA). The adsorbent tubes were 11.5 cm long and had an internal diameter of 4 mm. Tubes were packed with Carbotrap F, Carbotrap C, Carbotrap B and Carboxen 569 which is suitable to collect volatile compounds (C_2 and larger) in aqueous samples. Prior to use, the tubes were conditioned at 300°C for 40 min to eliminate impurities that might be in the tubes.

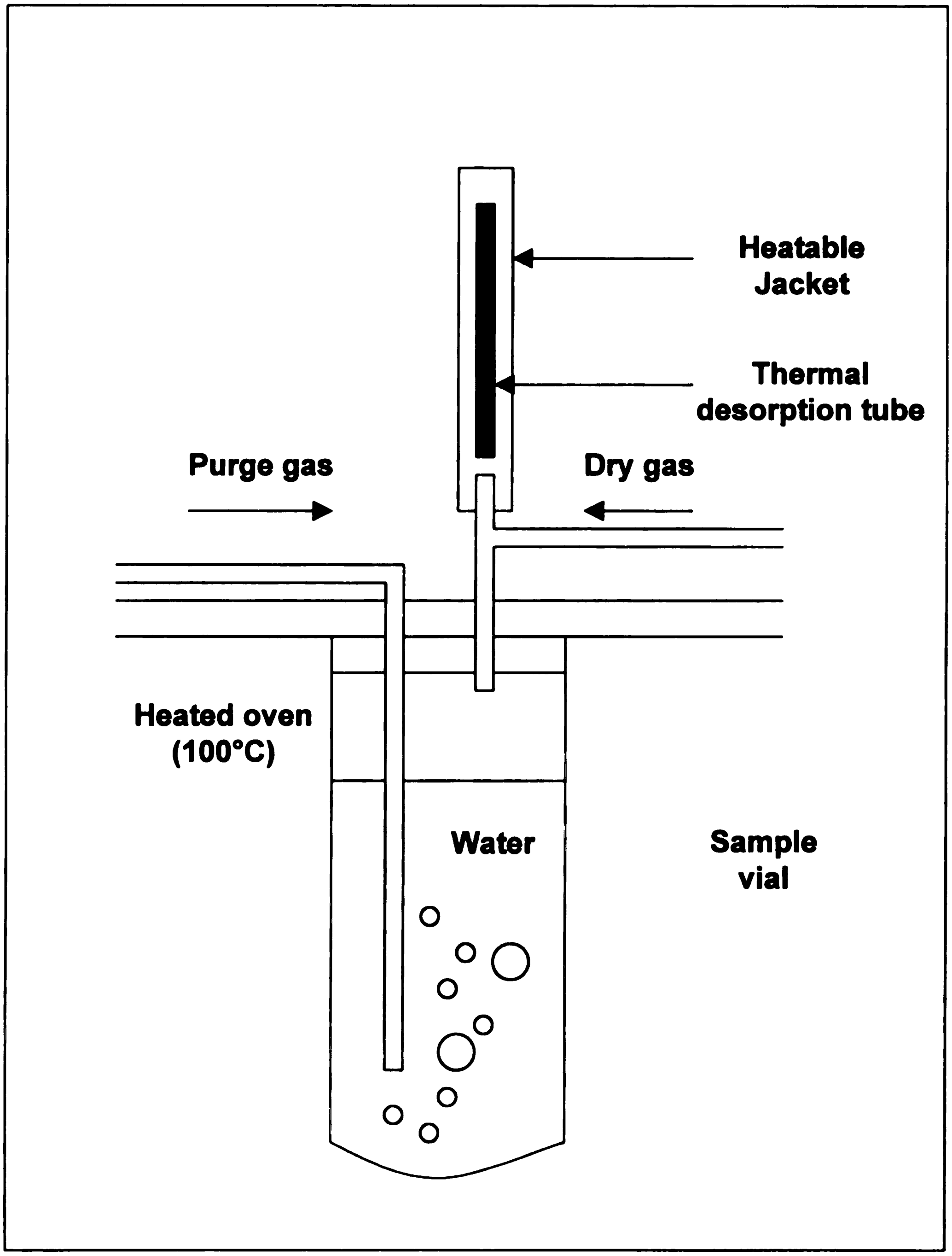


Figure 15 Thermal stripper and thermal desorption system used in Preparation of water samples

Volatiles were desorbed from sample tubes using a thermal desorption unit (Model 890, Dynatherm Analytical Instruments Inc., Kelton, PA) which was connected to a gas chromatograph (Model 5890, Hewlett Packard Co., Chicago, IL) and interfaced with the mass selective detector (Model HP 5970, Hewlett Packard Co., Chicago, IL).

The following conditions were used for thermal desorption of the volatile compounds found in the water samples. Helium was used as a carrier gas at a flow rate of 10 ml/min at 15 psi. The desorption temperature was set at 280°C (for 6 min), and the temperature of the valve and transfer lines was set at 250°C. After analysis, the tube was heated to 300°C for 40 min in the preparation path to remove all impurities prior to reuse.

The following conditions were optimized for the GC-MS analysis: the gas chromatograph was equipped with a SPB-5 non-polar fused silica capillary column (30 m (length) x 0.32 mm (internal diameter), Supelco Inc., Bellefonte, PA) of 1 μm film thickness. Initial temperature was set at 40°C and held for 6 min, followed by an increase of temperature of 20°C/min to 150°C and 30°C/min to 250°C, where it was finally held for 20 minutes. The solvent delay was 5 minutes and the cycles per second were 1.70. Helium was used as a carrier gas with a flow rate of 5 ml/min with a split ratio of 2.0. The temperature at the injection port was set at 220°C and the temperature of the transfer line between the GC and MS was 250°C. A 1 m (length) x 0.32 mm (internal diameter) Hydroguard FS deactivated column (Restex Co., Bellefonte, PA) was used as the transfer line. The total ion chromatogram peaks and the individual ion profiles were integrated, based on the integrator events set up with 0.02 as width, 1 as threshold and 5,000 as area reject.

The GC was interfaced with the mass selective detector (HP 5970) to focus on nonanal in the water samples. Selective Ion Monitoring (SIM) was performed to improve system selectivity and sensitivity. Mass constants of m/z 41, 43, 55, 56, 57, 70 and 98 were selected and used for nonanal identification.

Nonanal was identified using the previously described process. Quantitative analysis of nonanal in the water samples, prior to and after storage, was carried out. A calibration curve was established using an external standard. A dilution series of 2 to 20 ppm of nonanal in water (HPLC grade, J.T. Baker Inc., Phillipsburg, NJ) was prepared and 1 μl of the standard was injected into the absorbent tubes using a 5 μl syringe (Hamilton Co., Reno, NV). Triplicate runs were performed prior to establishing the standard calibration curve of nonanal in the water. The amount of nonanal present in the water samples was estimated based on the relationship between nonanal concentration and area response.

2.4. Sensory evaluation of water samples packaged in glass and HDPE containers

2.4.1. Panelist selection

Panelists were selected based on their ability to detect off-odor. A ranking test was performed using water samples, which had four different off-odor levels. The water samples were prepared by adding a sample of HDPE to distilled water (HPLC grade, J.T. Baker Inc., Phillipsburg, NJ) in a 40 ml vial, which was closed with a Teflon seal cap (Supelco Inc., Bellefonte, PA). The vials were then stored at 70 ± 2°C for three weeks to increase the transfer of off-odor compounds into the aqueous phase. The four aqueous samples included water samples without HDPE, and water samples with 0.3, 0.9 and 1.8 g of HDPE added. After three weeks, the aqueous samples were equilibrated at room temperature for 24 hours before evaluation by the taste panel. Panelists were asked to sniff the samples and rank them in order of their off-odor level. The panelists who ranked the samples correctly or inverted only adjacent pairs were selected (Meilgaard et al., 1991). Ten panelists were selected for further training and evaluation.

2.4.2. Sensory evaluation of water samples

After three and six months of storage at 38 ± 2°C and 65 ± 5% RH in the controlled environmental chamber, the water packed in the four HDPE containers was served to individual panelists for sensory evaluation. In addition, water packaged in a glass container and stored under identical conditions was used as the reference sample. Water samples which were filled into the containers and equilibrated for 24 hours at ambient temperature were also subjected to sensory evaluation as initial controls.

A Difference-from-Control test was conducted to evaluate the odor difference between the water packaged in a glass container (reference sample) and the respective HDPE containers. All sensory tests were conducted in the sensory laboratory in the Food Science Department, Michigan State University

(East Lansing, MI). Four sessions of the test were conducted within two days using the same panelists.

Water samples from the respective treatments were presented to the panelists. Each sample contained 50 ml of water and was served in a one ounce premium grade polypropylene (PP) medicine cup. The panelists were asked to sniff and taste the samples, and then to compare the odor intensity with the reference sample. The panelists were pre-trained to become familiarized with the test and the water samples prior to the actual test. Purified distilled water was used for oral rinsing between samples. The degree of off-odor or off-odor intensity was ranked from 1-5 (Table 5). A higher number indicates a greater difference from the reference sample. A sample sensory questionnaire and consent form is shown in Appendix B.

Table 5 Sensory ranking for Difference-from-Control test of water samples

Numerical score	Odor intensity
0	No difference
1	Very slight difference
2	Slight difference
3	Moderate difference
4	Large difference
5	Extreme difference

The mean and standard error of each treatment difference was reported. Analysis of Variance (ANOVA) and Duncan's New Multiple Range test were performed to determine the significant difference ($p<0.05$) between the samples using the SPSS 10.0 statistical package (SPSS Inc., Chicago, IL).

3. Determination of the oxidation levels of the HDPE surfaces using surface analysis techniques

3.1. Determination of oxidation levels of the HDPE surfaces using Fourier Transform-Infrared (FT-IR) spectrophotometer

To determine the extent of oxidation on the container internal surface, the inside surfaces of the container samples were examined using FT-IR spectrophotometric analysis. Since the container samples were too thick to allow a simple infrared transmission, the Horizontal Attenuated Total Reflectance (HATR) technique was employed with the Fourier Transform-Infrared (FT-IR) Spectrophotometer model Spectrum 1000 (Perkin Elmer Co., Norwalk, CT). The 45° Zinc Selenide (ZnSe) crystal (Density = 5.27 g/cm^3, Reflective Index at 1000 cm^{-1} = 2.4, Transmission range = 17000-650 cm^{-1}) was installed in the HATR apparatus (Perkin Elmer Co., Norwalk, CT). There are twelve reflections at the crystal angle of 45°.

The sidewalls of the container samples were cut into approximately 6 x 4 cm samples in order to cover the surface of the crystal. The samples were placed and securely mounted on top of the crystal surface to eliminate air between the two surfaces. Scanning was carried out in the range of 4000-650 cm^{-1} wavenumber. For each measurement, 16 scans were accumulated at 4

cm^{-1} resolution. In addition, background scanning was performed using the same crystal prior to analysis of the HDPE sample.

From the spectra, the oxidation indices were calculated using the absorption values at 1720 cm^{-1} and 2660 cm^{-1} which are the absorption regions for carbonyl groups (-C=O) and allyl groups (-CH), respectively.

$$\text{Oxidation index} = \frac{\text{Absorption value at } 1720\ cm^{-1}}{\text{Absorption value at } 2660\ cm^{-1}}$$

The analysis was carried out before and after the containers were stored at 38 ± 2°C for three and six months. Triplicate samples of each container sample were subjected to the evaluation. Statistical analysis, i.e. ANOVA, and Duncan's New Multiple Range test were also carried out at a 95% confidence level.

3.2. Atomic oxygen concentrations of the HDPE surfaces using Electron Spectroscopy for Chemical Analysis (ESCA) measurement

The inside surfaces of the four HDPE container samples were subjected to Electron Spectroscopy for Chemical Analysis (ESCA) measurement in order to determine the extent of surface oxidation. The atomic oxygen level on the surface of the containers was then calculated. The analysis was carried out before and after the containers were stored at 38 ± 2°C for three and six months.

The container samples were cut into small pieces before placing into a sample holder. Surface analysis was performed using a Physical Electronics

ESCA spectrometer model PHI5400 (Perkin Elmer Co., Norwalk, CT) equipped with a standard magnesium X-ray source which was operated at 300 W (15 kV and 20 mA). Data was collected in the Fixed Analyzer Transmission mode, utilizing a position sensitive detector, and a hemispherical analyzer. The elemental composition of the surface was determined from survey spectra collected using a pass energy of 89.45 eV. High-resolution spectra of the elements were obtained using a pass energy of 22.5 eV and a step size of 0.1 eV. All binding energies were referenced to adventitious carbon (C 1s = 284.6 eV) and were measured with a precision of ± 0.1 eV. Quantitative measurement, i.e. peak area, was determined using the Perkin Elmer software.

Chapter III

RESULTS AND DISCUSSION

1. Analysis of the off-odors released from HDPE containers using the electronic nose system and GC-MS analysis

1.1. Sensitivity and selectivity of the metal oxide sensors used in the electronic nose system

Twelve metal oxide sensors are used in the Fox 3000 electronic nose system. Each sensor partially responds to a specific group of compounds such as alcohols, aldehydes, etc. A similar odor response profile is expected to be obtained from the same chemical standard under similar testing conditions, unless sensor drift occurs. Figure 16 shows the responses of six metal oxide sensors to three different compounds. All sensors responded to all compounds at different levels. Using a greater number of sensors, i.e. an array of 4-32 sensors with slightly different response, helps improve system selectivity. Sensitivity can be determined based on the lowest detection threshold that the sensors respond to, in regards to the selected off-odor compound.

Nonanal is a known off-odor compound with a low odor threshold that can be found at significant levels in the volatile headspace of HDPE container samples using Gas Chromatograph-Mass Spectrometer (GC-MS) (Ho et al., 1996). The odor detection threshold of nonanal in water is 1 ppb (Leffingwell and Leffingwell, 1991). Due to its low odor threshold, it is possible to obtain a good sensor response even at a very low concentration. Thus, the sensitivity of the metal oxide sensors used in the Fox 3000 electronic nose system was determined using nonanal.

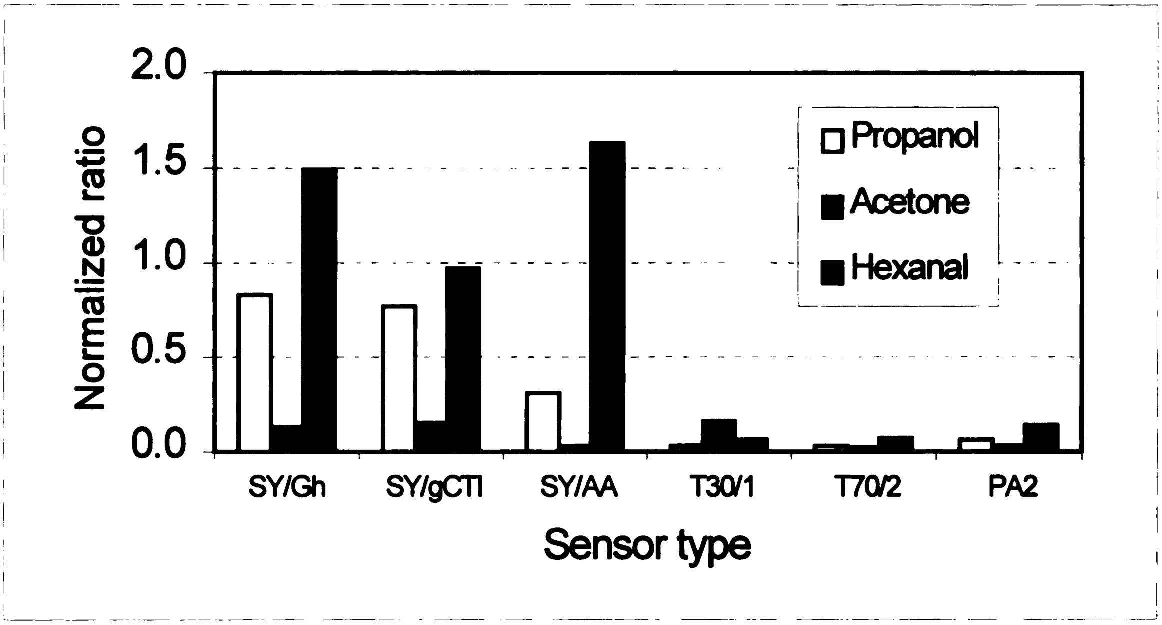
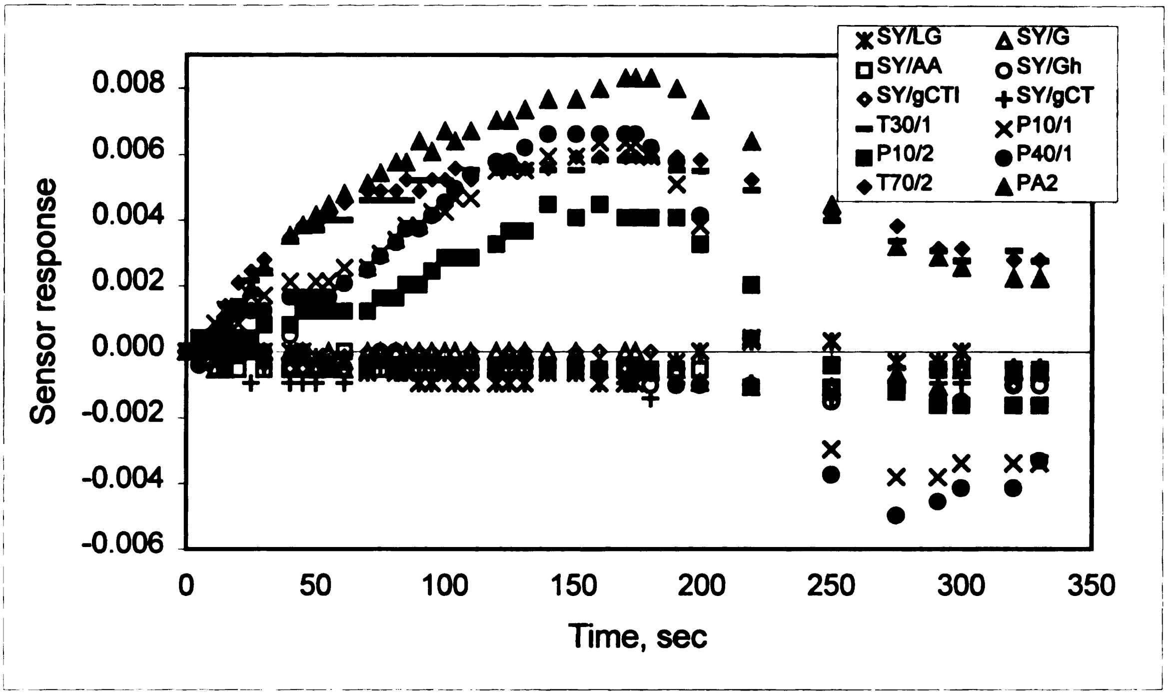
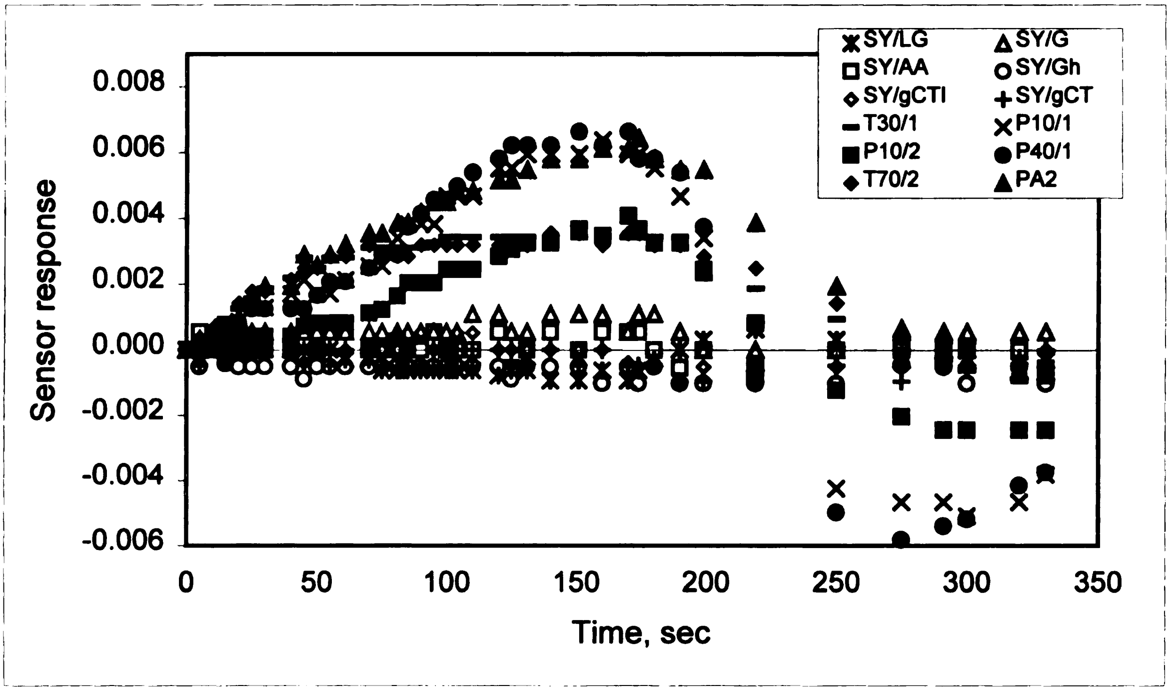


Figure 16 Responses of selected sensors to propanol, acetone and hexanal

Figure 17 shows the sensor responses obtained from highly purified water (HPLC grade) and triacetin. The sensors show little reaction to water and triacetin. The sensor responses from the two solvents were very low compared to the responses obtained from 1% nonanal (Figure 18). Using these two solvents helped to minimize the effect of sensor response interference. Nonanal dissolved slightly better in triacetin than in water. At high nonanal concentration, the heterogeneous phase between nonanal and water was visually observed. Therefore, triacetin was used as the dilution solvent in this study.



a) 1 ml of triacetin incubated at 120°C, 15 min



b) 1 ml of water (HPLC grade) incubated at 120°C, 15 min

Figure 17 Change in the twelve sensor responses over time (350 sec acquisition) from 1 ml of triacetin and water (HPLC grade) incubated at 120°C, 15 min.

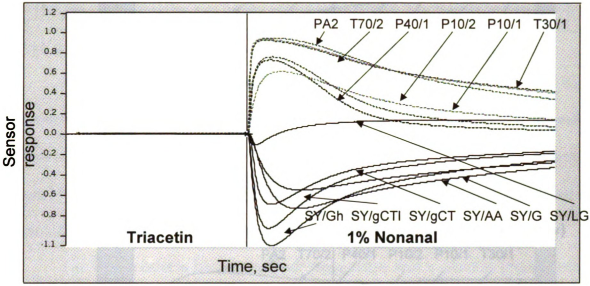
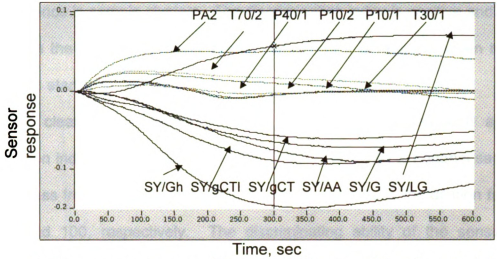


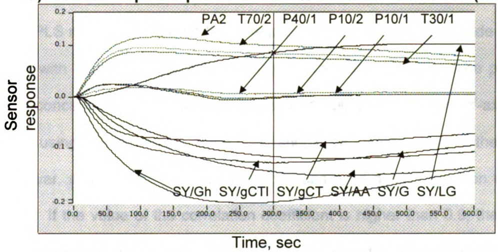
Figure 18 Sensor responses of pure triacetin and 1% nonanal in triacetin (volume/volume)

Figure 19 presents the sensor response profiles of 0.001, 0.01 and 1% nonanal in triacetin (volume/volume). Due to the higher concentration of nonanal in the sample headspace, the sensor response intensities obtained from 1% nonanal were higher than 0.01 and 0.001% nonanal, respectively. Thus, an increase in sample concentration increased the reaction between the metal oxide sensors and nonanal. If the concentration is too low to react with the metal oxide on the sensor surface, the detection threshold of the sensors cannot be determined.

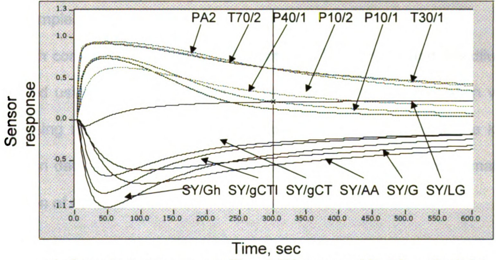
Principal Components Analysis (PCA) reduces the number of variables represented by the sensor responses, and transforms the multiple dimensional data into common vectors. The discrimination index provides information relative



a) Sensor response profile of 0.001% nonanal in triacetin (v/v)



b) Sensor response profile of 0.01% nonanal in triacetin (v/v)



c) Sensor response profile of 1% nonanal in triacetin (v/v)

Figure 19 Sensor response profiles of 0.001, 0.01 and 1% nonanal in triacetin (v/v) to the difference in sample clusters. The discrimination index is positive and close to 100 when the groups are easily discriminated, but it is negative when two or more groups start to overlap.

PCA clearly discriminated between these three samples with a high discrimination index (93) (Figure 20.1). The 0.001% and 0.01% nonanal samples separated less from each other than the 1% nonanal because the dilution factors were 10 and 100, respectively. The discriminating ability of the sensors is dramatically reduced for compounds at low concentration.

The PLS model is based on linear regression, and is used to provide more information with regards to quantitative analysis, i.e. concentration. The plot of the known concentration (X-axis) versus the predicted concentration (Y-axis) is established using a PLS model. Each point should be located close to the Y=X line. However, a spread on the Y-axis may be observed due to variation within the sample. If the value of the correlation coefficient is higher than 0.9, the PLS model is considered valid and can be used to estimate the concentration of an unknown sample.

A high correlation coefficient (0.99) between 0.001, 0.01 and 1% dilutions, was obtained using PLS as illustrated in Figure 20.2. The concentration values predicted using the PLS model were quite close when compared to the known concentration data. Thus, the PLS model was successfully used to estimate the concentration of nonanal in unknown samples between 0.001-1.0%.

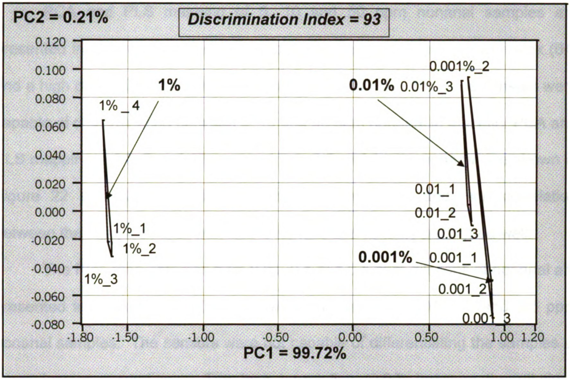


Figure 20.1 PCA of 1.0 ml of 0.001, 0.01 and 1% nonanal in triacetin (v/v)

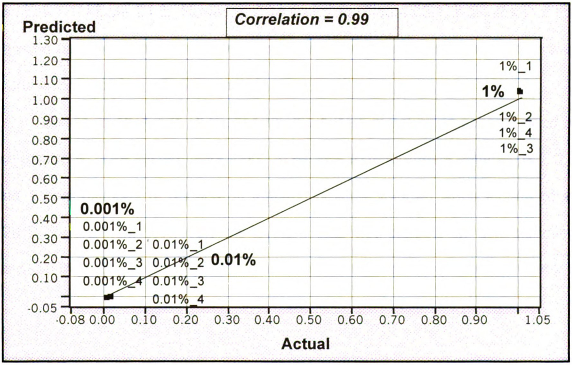


Figure 20.2 PLS of 1.0 ml of 0.001, 0.01 and 1% nonanal in triacetin (v/v)

PCA and PLS mapping of 5, 10 and 50 ppm nonanal samples are presented in Figures 21.1 and 21.2. As shown, a good discrimination index (64) and a high correlation were obtained from these dilutions. Thus, the sensors were capable of discriminating between 5, 10 and 50 ppm nonanal in triacetin. PCA and PLS mappings of 1, 5 and 10 ppm and 0.1, 0.5 and 1 ppm nonanal are shown in Figure 22 and 23, respectively. Good discrimination, and high correlation between the samples indicates that the metal oxide sensors performed well.

The PCA map obtained from 0.01, 0.1 and 0.5 ppm dilutions of nonanal are presented in Figure 24.1. Overlap was found between 0.01, 0.1 and 0.5 ppm nonanal samples. The sensors were not capable of differentiating the samples at these low concentrations. The high correlation (0.99) between the dilutions indicates that estimation of the unknown concentration may be obtained by PLS as shown in Figure 24.2. However, PCA mapping (Figure 23.1) indicates that the sensors had reached their performance limit, even though good correlation was found when applying a PLS regression.

Based on PCA and PLS analysis, the twelve metal oxide sensors used in the electronic nose system were found to be able to differentiate between 0.1, 0.5 and 1 ppm dilutions of nonanal in triacetin (volume/volume) when incubated at 120°C for 15 min. However, the system was not capable of discriminating between 0.01, 0.1 and 0.5 ppm dilutions of nonanal in triacetin (volume/volume).

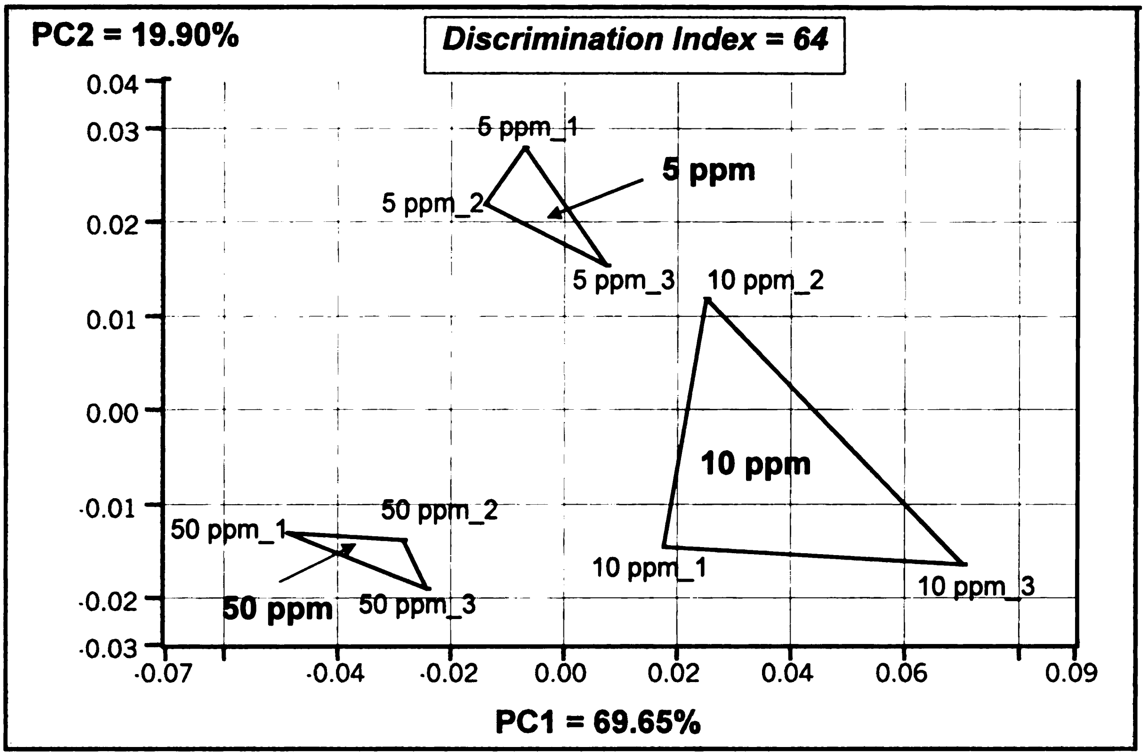


Figure 21.1 PCA of 1.0 ml of 5, 10 and 50 ppm nonanal in triacetin (v/v)

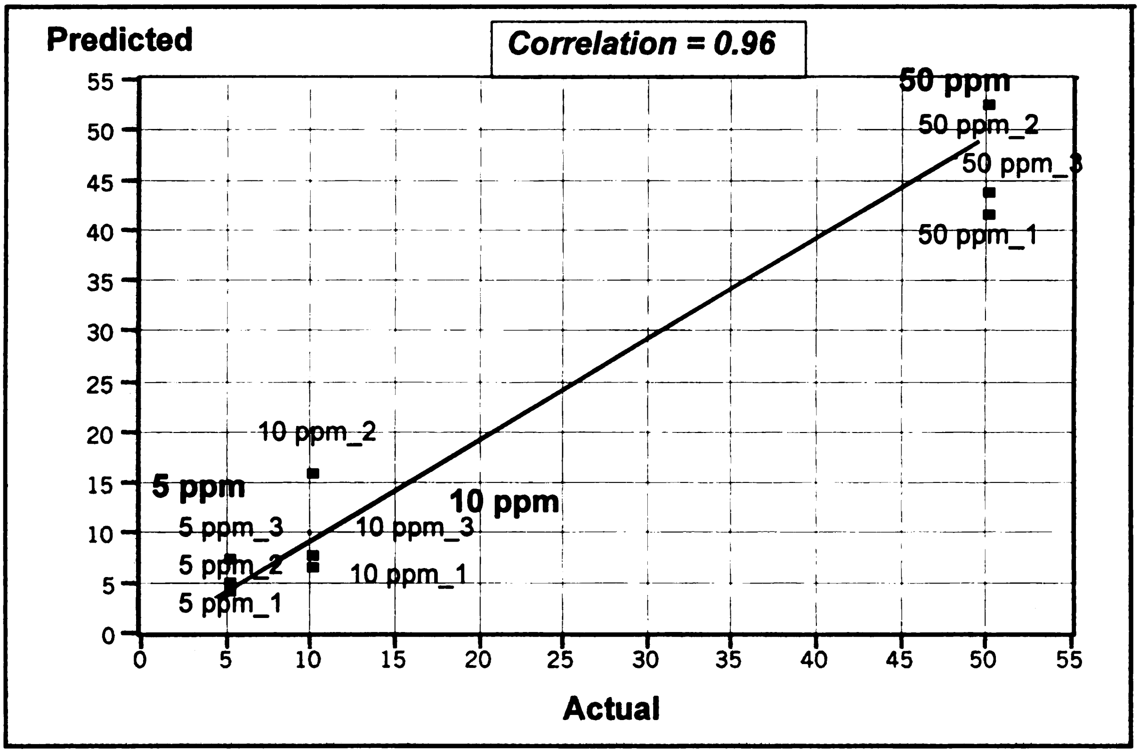


Figure 21.2 PLS of 1.0 ml of 5, 10 and 50 ppm nonanal in triacetin (v/v) (0.96)

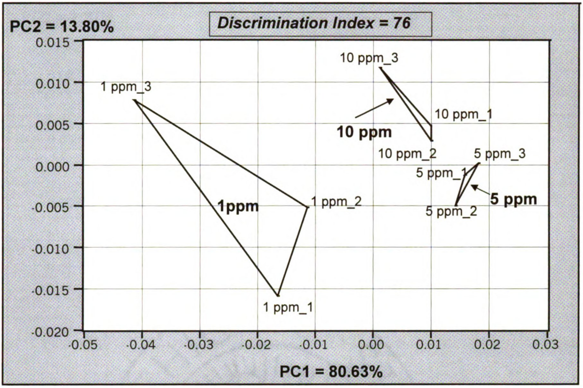


Figure 22.1 PCA of 1.0 ml of 1, 5 and 10 ppm nonanal in triacetin (v/v)

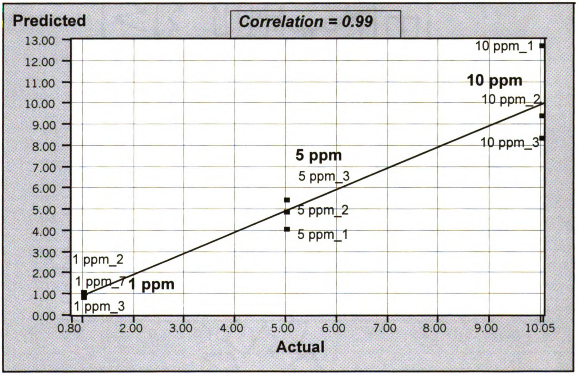


Figure 22.2 PLS of 1.0 ml of 1, 5 and 10 ppm nonanal in triacetin (v/v)

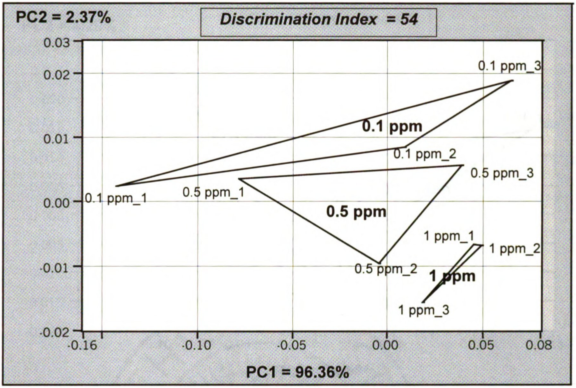


Figure 23.1 PCA of 1.0 ml of 0.1, 0.5 and 1 ppm nonanal in triacetin (v/v)

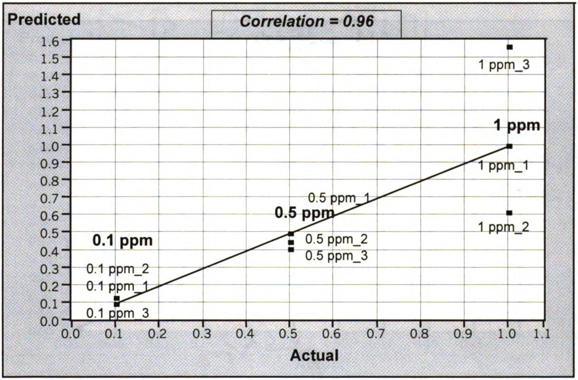


Figure 23.2 PLS of 1.0 ml of 0.1, 0.5 and 1 ppm nonanal in triacetin (v/v)

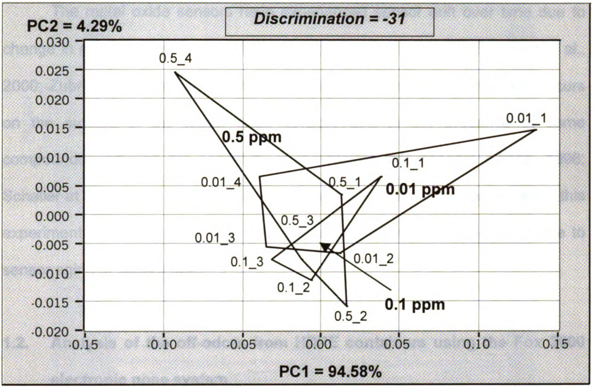


Figure 24.1 PCA of 1.0 ml of 0.01, 0.1 and 0.5 ppm nonanal in triacetin (v/v)

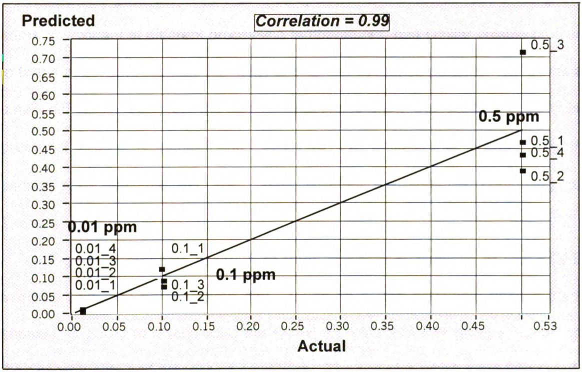


Figure 24.2 PLS of 1.0 ml of 0.01, 0.1 and 0.5 ppm nonanal in triacetin (v/v)

The metal oxide sensors have experienced sensor drift over time due to change in electrical resistance (Mielle, 1996; Bartlett et al., 1997; Steinhart et al., 2000; Zubritsky, 2000). In addition, the possibility of irreversible reaction occurs on the surface of the metal oxide sensors due to the presence of some compounds, reducing the sensitivity of the metal oxide sensors (Mielle, 1996; Schaller et al., 1999). The metal oxide sensors were over one year old when this experiment was conducted. Some loss of sensitivity may have occurred due to sensor aging or sensor drift.

1.2. Analysis of the off-odors from HDPE containers using the Fox 3000 electronic nose system

Sensor response profiles from the respective HDPE container samples are presented in Figure 25. The HDPE samples, which were fabricated using the same antioxidant at different processing temperatures, had similar volatile profiles in terms of sensor response intensity, and sensor response pattern. There was a small difference between the sensor responses from the container samples produced using α-Tocopherol and Irganox 1010 as antioxidants. A slightly higher sensor response intensity was obtained from the samples containing α-Tocopherol.

Figure 26 presents the PCA of three replicate evaluations of four HDPE samples analyzed on the same day. Using PCA, the electronic nose system showed its ability to discriminate the HDPE samples into four groups, based on their constituents and processing conditions. The samples which were fabricated

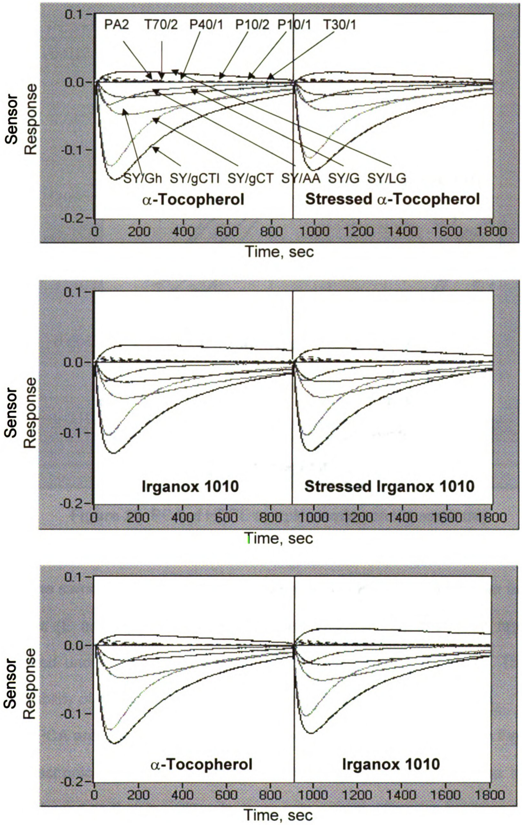


Figure 25 Sensor response profiles of four HDPE samples

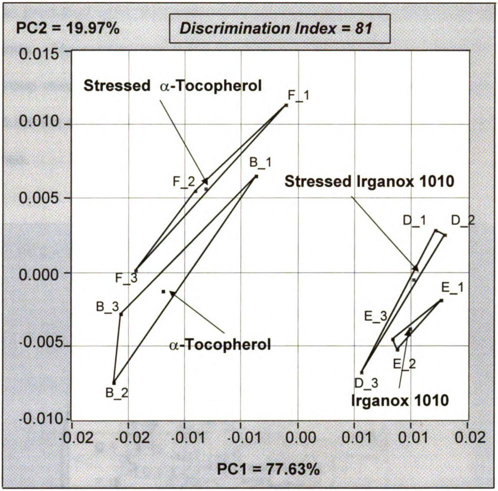


Figure 26 PCA of HDPE samples testing on the same day

using the same antioxidant (B and F), were close, while separated from the other samples (E and D). Similar results were obtained from the three replicates, evaluated under the same testing conditions, on six-alternate days. Thus, the repeatability of the Fox 3000 electronic nose system was demonstrated.

PCA analysis of the data from the six-day evaluation is shown in Figure 27. The electronic nose system clearly differentiated the HDPE samples into two groups based on their constituents, there was a great difference between the odor generated from the different compositions. However, there was overlap between samples produced using the same antioxidant at normal and abusive temperature conditions. The overlap may have resulted from higher variation within this larger data group resulting in data spread. Sensor drift may also have occurred. Drift will reduce the sensitivity of the system and can result in a small change in sensor response.

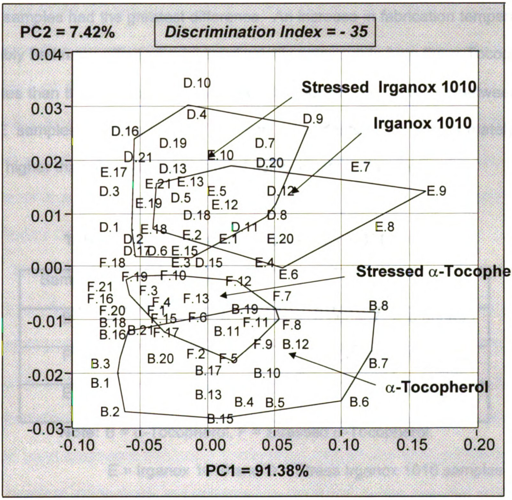


Figure 27 PCA of four HDPE samples; 3 replicates data from 6 days analysis

Group distance is another way to compare the similarity between the samples. The group distance is the Euclidean distance between the groups. The greater the distance, the greater the difference between the samples. Table 6 presents the group distances between the four HDPE clusters as shown in Figure 26. The lowest and highest distances were obtained from group D (Stressed Irganox 1010) and group E (Irganox 1010), group B (α-Tocopherol) and group D (Stressed Irganox 1010), respectively. Thus, stressed Irganox 1010 and Irganox 1010 samples had the least difference, while α-Tocopherol and stressed Irganox 1010 samples had the greatest difference. An increase in fabrication temperature probably had more effect on release of volatile compounds from the α-Tocopherol samples than the Irganox 1010 samples. In addition, the distances between the HDPE samples produced using different antioxidants were approximately ten times higher than the samples produced using similar antioxidants.

Table 6 Group distances between four HDPE groups

Sample	B	F	E	D
B	-	0.000065	0.000487	0.000495
F	-	-	0.000422	0.000383
E	-	-	-	0.000021

Note: B = α-Tocopherol, F = Stressed α-Tocopherol,

E = Irganox 1010 and D = Stress Irganox 1010 samples

2. Analysis of the off-odors released from HDPE containers by GC-MS analysis

2.1. Identification of specific volatile organic compounds associated with off-odors from HDPE containers

Identification of the volatile compounds from the four HDPE container samples was carried out using a Thermex Thermal Desorption unit interfaced with a Time-of-Flight GC-MS system (LECO® Pagasus II). More than 40 compounds were identified in the headspace volatiles ranging from C_2 -C_{16} molecular weight, consisting of alkanes, alkenes, aldehydes, olefins and paraffins (Appendix C). These results agree with those of Bravo and Hotchiss (1993), Ho et al. (1994) and Yam et al. (1996) who reported that alkanes and alkenes made up a significant portion of the thermal/mechanical degradation fragments of polyethylene, as identified by GC-MS analysis.

The intermolecular transfer mechanism, proposed by Tsuchiya and Sumi (1968) can be used to explain the generation of the volatile compounds during thermal degradation of polyolefin. The volatile compounds, such as 1-decene, 1-tetradecene, undecane, nonanal, decanal and undecanal can be formed through an intramolecular transfer mechanism followed by β-scission. In addition, random bond breakages can occur due to shear degradation so higher levels and more types of compounds are expected to be found during polymer extrusion. The breakages result from the entanglement of the polymer chains with consequent stress at certain points in the polymer chains sufficient to cause carbon-carbon bond scission (Scott, 1978; Hinsken et al., 1991).

The total ion chromatograms, i.e. total ion responses as a function of retention time from the four container samples, are presented in Figure 28. There was a significant difference between the total ion chromatograms obtained from the samples produced with the different antioxidants, in both ion intensity and in the specific compounds present in the headspace. There was similarity in the volatile headspace of HDPE samples produced using the same antioxidant. Higher ion intensities were obtained from α-Tocopherol samples than from the Irganox 1010 samples, and more compounds were present in the headspace of the α-Tocopherol samples. Not all these compounds have to be responsible for off-odor from the HDPE containers (Koszinowski and Piringer, 1986; Linssen et al., 1991; Kuijk and Warnar, 1993; Ho et al., 1996; Yam et al., 1996)

Ho et al. (1994) stated that odor threshold, molecular weight and polarity were three major factors involved in contribution to the release of off-odor compounds from HDPE containers. The lower the odor threshold, the easier it is for the consumer to detect off-odor. For example, the threshold levels of aldehydes and ketones are lower by at least three orders of magnitude than those of alkanes and alkenes (Table 3; Koszinowski and Piringer, 1986; Liffingwell and Liffingwell, 1991). Therefore, trace amounts of aldehydes or ketones may cause an off-odor problem (Koszinowski and Piringer, 1986; Linssen et al., 1991; Ho et al., 1994; Yam et al., 1996).

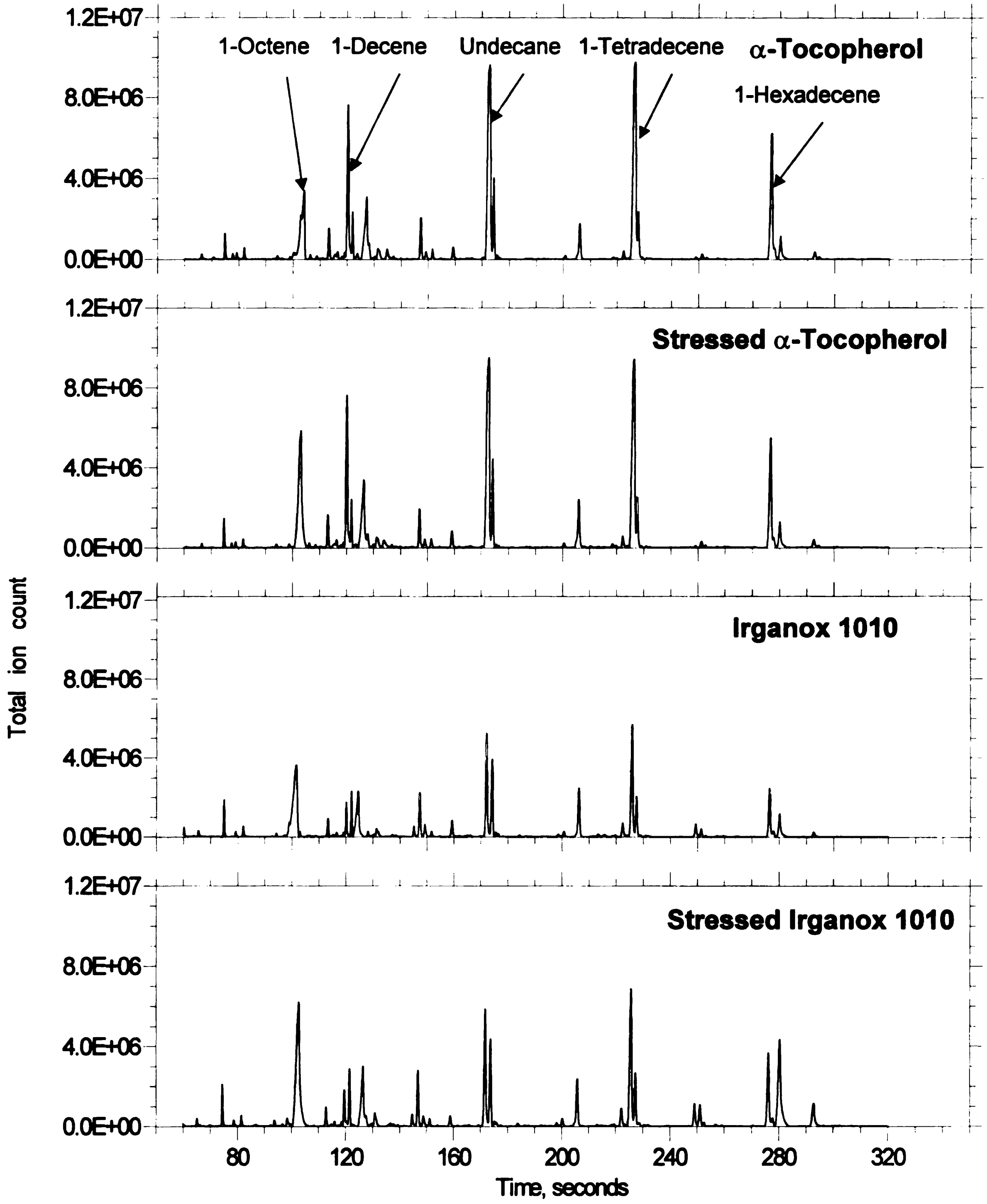


Figure 28 Total chromatograms obtained from four HDPE container samples

Molecular weight determines the rate at which odor compounds desorb from the polymer matrix to the gas phase, which then may further migrate into the contained food product. For a homologous series, the lower the molecular weight, the higher the volatility of the odor compounds. Highly volatile compounds, such as C_4-C_5, tend to escape to the gas phase and may not be at measurable levels following extended storage, while the lower volatile compounds have less tendency to release to the gas phase during storage.

Polar compounds have a greater tendency to escape from a nonpolar polymer matrix. Polar volatiles tend to be easily transferred from the polymer matrix into water leading to an off-odor problem. Aldehydes and ketones are relatively polar compared to hydrocarbon fragments, so they tend to migrate from polymer to water leading to an off-taste problem (Linssen et al., 1991). The most offensive odor compounds associated with the thermal degradation of polyethylene are ketones or aldehydes of specific molecular weight, which are not too volatile to evaporate from the surface during the blow molding process, but sufficiently volatile to desorb from the polymer matrix during storage (Ho et al., 1994; Yam et al., 1996).

As shown in Figure 28, 1-octene, 1-decene, undecane, 1-tetradecene and 1-hexadecene were found to be the dominant components, which confirmed that alkanes and alkenes were the major components found from thermal degradation of HDPE samples. The higher total ion count indicated that higher levels of the compounds were present in sample headspaces. Lower amounts of 1-octene, 1-decene, undecane and 1-tetradecene were found in the Irganox 1010 samples than the α-Tocopherol samples. Consequently, Irganox 1010 had better ability to prevent the release of breakdown products from HDPE thermal degradation than α-Tocopherol. The total ion counts of some aldehydes and ketones i.e. nonanal, were found in lower levels in the α-Tocopherol than Irganox 1010 samples. This indicates that α-Tocopherol had better ability to prevent of the formation of aldehydes and ketones than Irganox 1010.

During container fabrication, i.e. blow molding, polymer resins experience heat and shear energy, which can result in bond breakages (Conley, 1970; Scott, 1978; Hoff and Jacobsson, 1981; Hinsken et al., 1991; Ebewele, 2000). In addition, oxygen is always present in the polymer since the solubility of oxygen in polyolefin is only a little lower than in a hydrocarbon liquid (Hinsken et al., 1991). The free radicals generated can attack other polymer molecules or react with oxygen to form oxygen containing volatile compounds such as aldehydes and ketones, causing off-odor and off-flavor (Linssen et al., 1991; Ho et al., 1994; Yam et al., 1996).

A list of aldehydes and ketones found in the four HDPE container samples is shown in Table 7. Saturated aldehydes such as hexanal, nonanal, decanal, undecanal and dodecanal were identified in all four HDPE samples. Butanal was the smallest aldehyde identified in the samples fabricated at normal temperature (174°C), but it was not identified from the samples fabricated at abusive temperature (204°C) conditions. Pentanal and hexanal were the smallest aldehydes identified from stressed Irganox 1010, and stressed α-Tocopherol

Table 7 Aldehydes and ketones identified in the four HDPE samples

Compound	HDPE sample			
	α-Tocopherol	Stressed α-Tocopherol	Irganox 1010	Stressed Irganox 1010
Aldehyde				
Butanal	✓	✗	✓	✗
Pentanal	✗	✗	✗	✓
Hexanal	✓	✓	✓	✓
Benzaldehyde	✓	✓	✓	✗
Nonanal	✓	✓	✓	✓
2-Nonenal	✗	✗	✓	✓
Decanal	✓	✓	✓	✓
Undecanal	✓	✓	✓	✓
Dodecanal	✓	✓	✓	✓
Ketone				
Methyl Isobutyl Ketone	✓	✓	✓	✓
2,2-Dimethyl, 3-Hexanone	✗	✗	✓	✗

Note: ✓ = compound found in the sample, ✗ = compound not found in the sample samples, respectively. Due to its high volatility, butanal could evaporate from the polymer matrix during container fabrication at high temperature.

Antioxidants prevent thermal degradation of HDPE by different oxidative mechanism (Burton and Ingold, 1986; Ho et al., 1994; Gugumus, 1994 and Yam et al., 1996). The general mechanism of phenolic antioxidants, such as Irganox 1010 and α-Tocopherol, to protect polymers against thermal oxidation has been proposed by Gugumus (1994). The phenolic ring acts as a hydrogen donor or as a chain-breaking donor (CB-D). The phenoxy radical formed in the process can react with a free radical as a chain-breaking acceptor (CB-A) to terminate the chain propagation. Polyphenolic antioxidants, such as Irganox 1010 follow this stabilization mechanism except they have more CB-D or CB-A sites. The transformation involves disappearance of propionate groups and the simultaneous appearance of cinnamate groups. For pyranophenolic antioxidants, such as α-Tocopherol, they are rapidly oxidized by alkylperoxyl radicals to the corresponding tocopheroxyl radical. Further oxidation of the tocopheroxyl radical in polyolefins leads to the formation of coupling and quinonoid type products, such as dihydroxydimers, spirodimers and trimers, as well as aldehydes (Al-Malaika and Issenhuth, 1999). The tocopheroxyl radical can be easily formed because extra stabilization can be provided by the pyran ring oxygen that allows further electron delocalization between the ring and the oxygen atom, forming a stable two triene structure (Burton and Ingold, 1986).

In addition, unsaturated aldehydes, such as benzaldehyde was found in all HDPE samples, except stressed Irganox 1010. 2-nonenal was identified in the two Irganox 1010 samples. 2-nonenal is a conjugated, unsaturated carbonyl compound with a very low odor threshold (0.08-0.1 ppb) in water (Leffingwell and Leffingwell, 1991). α-unsaturated aldehydes and ketones are believed to be responsible for the off-odor associated with thermal oxidation of polyethylene (Koszinowski and Piringer,1986; Bravo et al., 1992 and Ho et al., 1994). 2-nonenal may be a product of the oxidation reaction of 1-nonene by a free radical mechanism at the allylic position. A trace level (ppb) of 2-nonenal was also reported as an off-odor source in LDPE coated paperboard (Koszinowski and Piringer, 1986).

Two ketones, methyl isobutyl ketone and 2,2-dimethyl, 3-hexanone, were identified in the HDPE samples. Methyl isobutyl ketone is an organic solvent normally used in polymer fabrication (ASTM E1870-98). Since it was identified in all HDPE samples, it may be present as a processing contaminant. The area responses significantly decreased over the three day analysis period. Methyl isobutyl ketone may be volatile enough to flash off during storage, and thus its off-odor effect would be minimized.

A trace amount of 2,2-dimethyl, 3-hexanone was identified in the Irganox 1010 sample, but was not found in the α-Tocopherol, or stressed Irganox 1010 samples. Thus, it may be a breakdown product of the oxidation reaction of Irganox 1010, but too volatile to remain at high fabrication temperature.

Figures 29-32 illustrate the overlay plots of the total chromatograms of the four HDPE samples at four retention time intervals; 65-95 sec., 95-135 sec., 135-190 sec. and 190-290 sec., respectively. There is a little shift between the retention time of each sample due to the difference in injection time.

Comparisons between the total chromatograms from the HDPE samples produced using the same antioxidants are shown in Figure 29a, 30a, 31a and 32a at a time interval of 65-290 sec. There was similarity in the HDPE samples produced using the same antioxidant. The low molecular weight compounds, which had high volatility, eluted prior to the high molecular weight compounds. Several low molecular weight volatile compounds, i.e. acetic acid (70.7 sec), were identified in the α-Tocopherol sample, but not in the stressed α-Tocopherol. Due to their volatility, the low molecular weight compounds may escape from the polymer matrix, or be transformed to intermediary products in containers produced at high temperature.

The formation of acetic acid during thermal oxidation of PE was reported by Bevilacqua et al. (1961). The authors found that the generation of organic acid depended on the temperature and crystallinity of the samples. In addition, organic acids were formed to a greater extent in HDPE than LDPE (Hoff and Jacobsson, 1981). Bravo and Hotchkiss (1993) studied the release of volatile compounds during heating of polyethylene in the presence of oxygen at 150-300°C for 5-15 min. The authors concluded that the amount and types of volatile compounds released from polyethylene are affected by temperature and heating time.

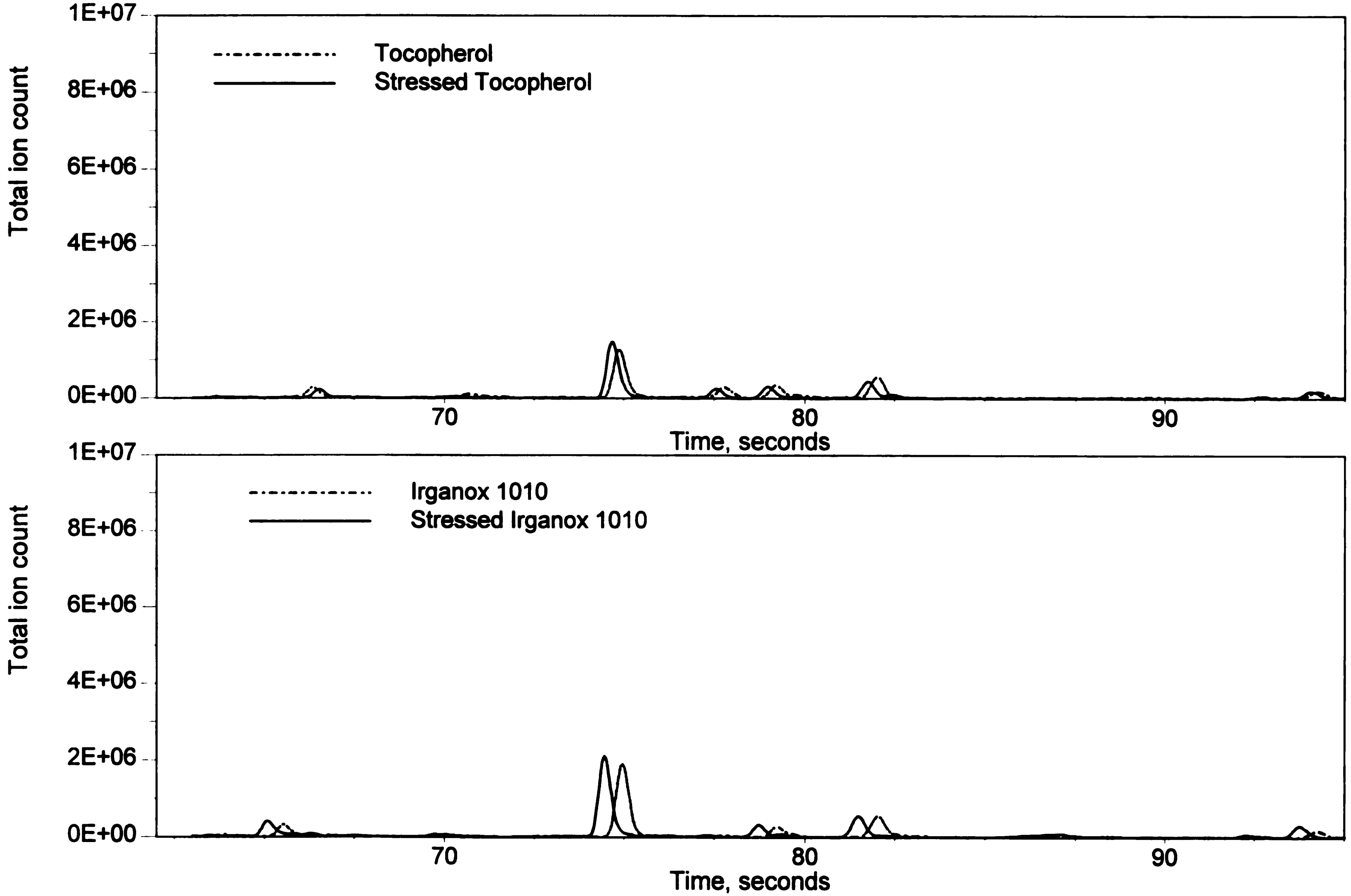


Figure 29(a) Total chromatogram of four HDPE samples (65-95 sec.)

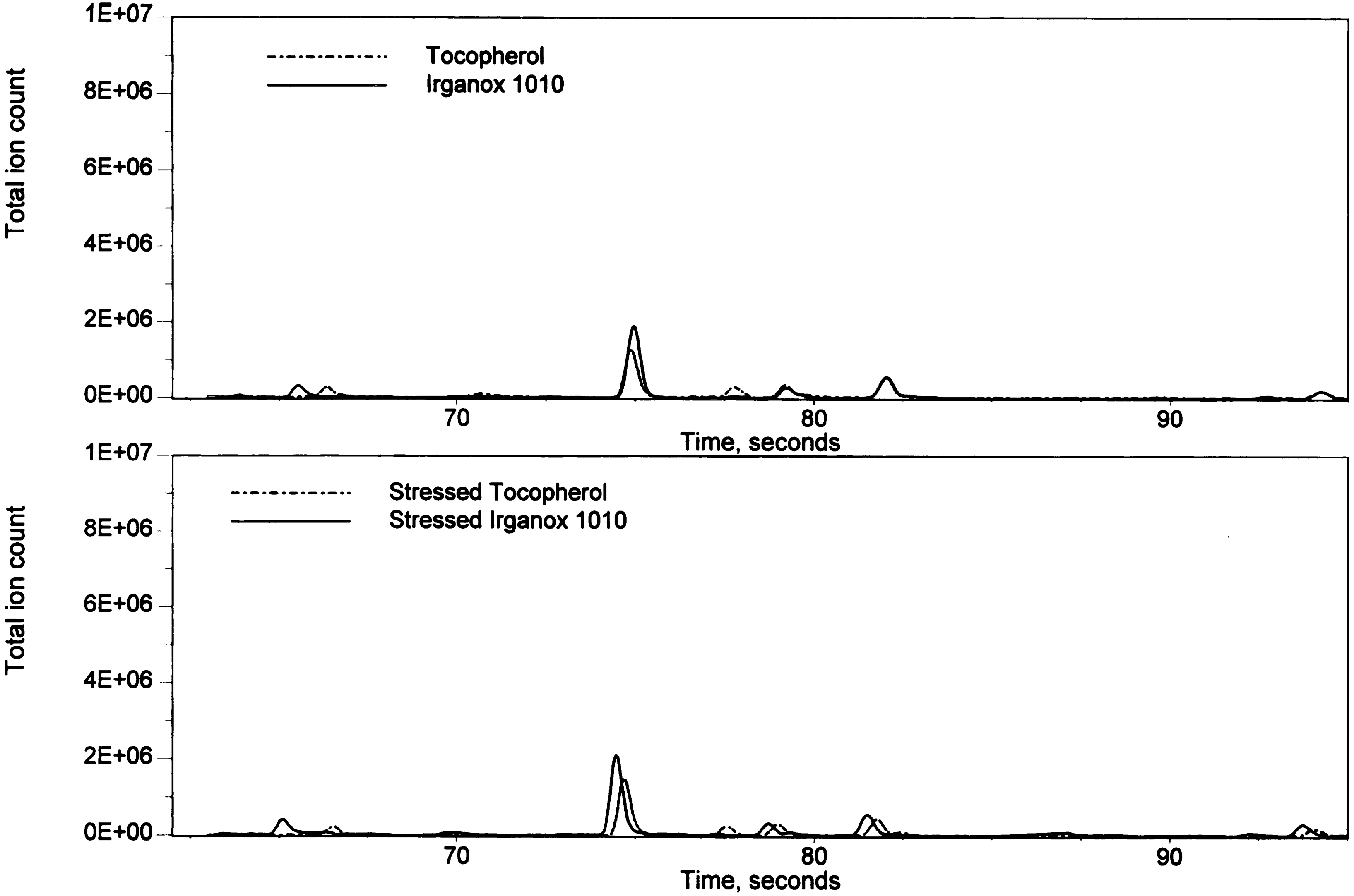


Figure 29(b) Total chromatogram of four HDPE samples (65-95 sec.)

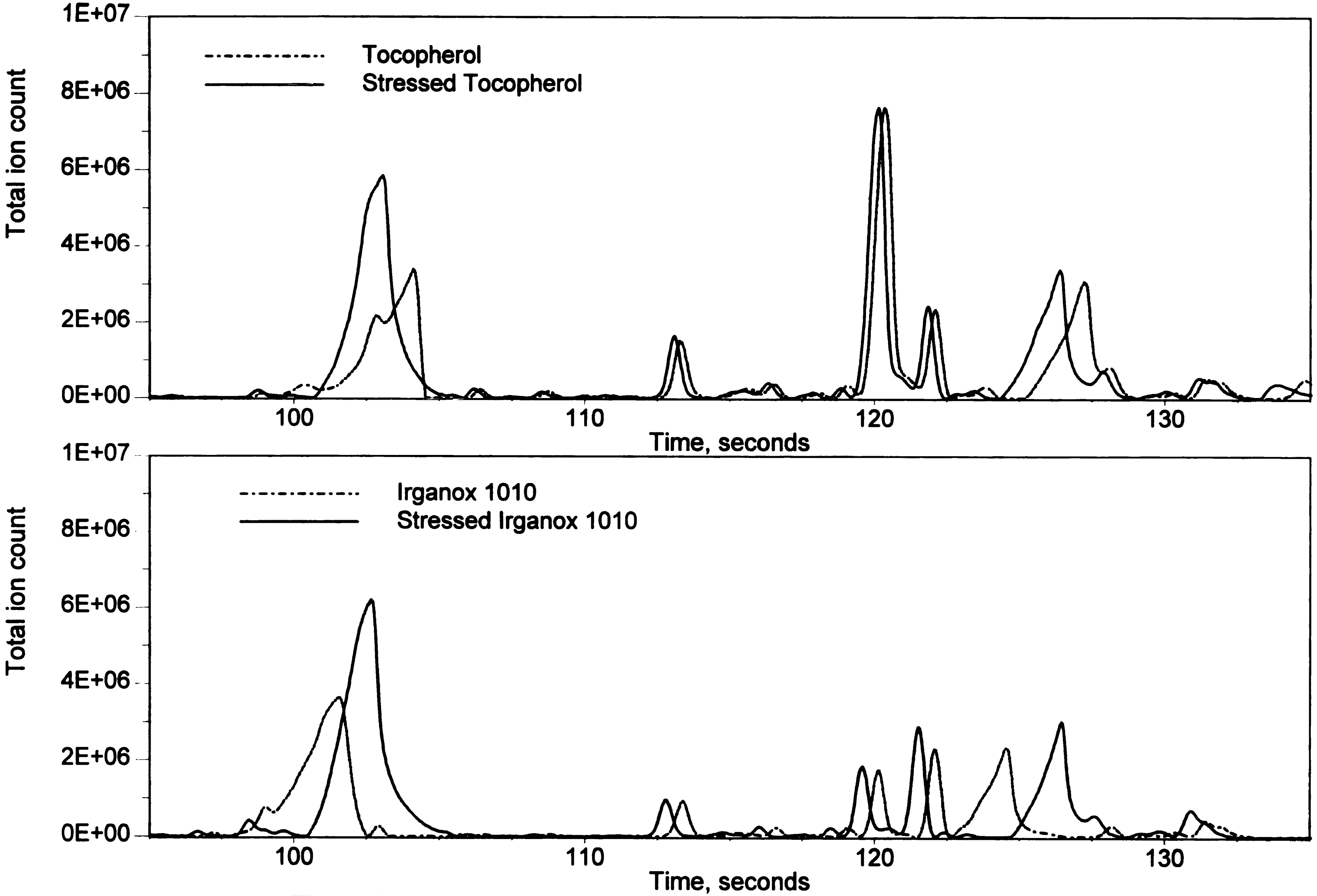


Figure 30(a) Total chromatogram of four HDPE samples (95-135 sec.)

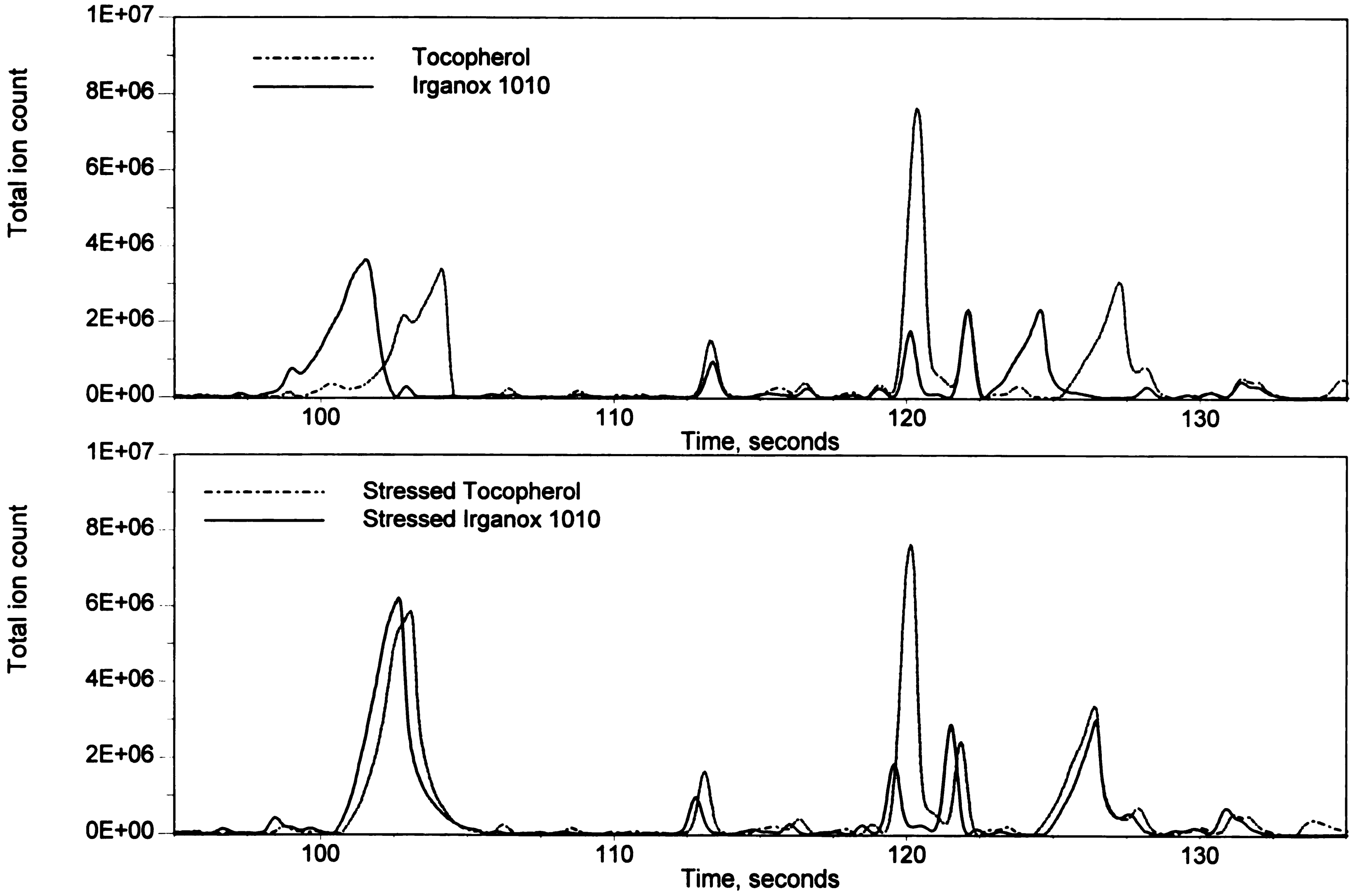


Figure 30(b) Total chromatogram of four HDPE samples (95-135 sec.)

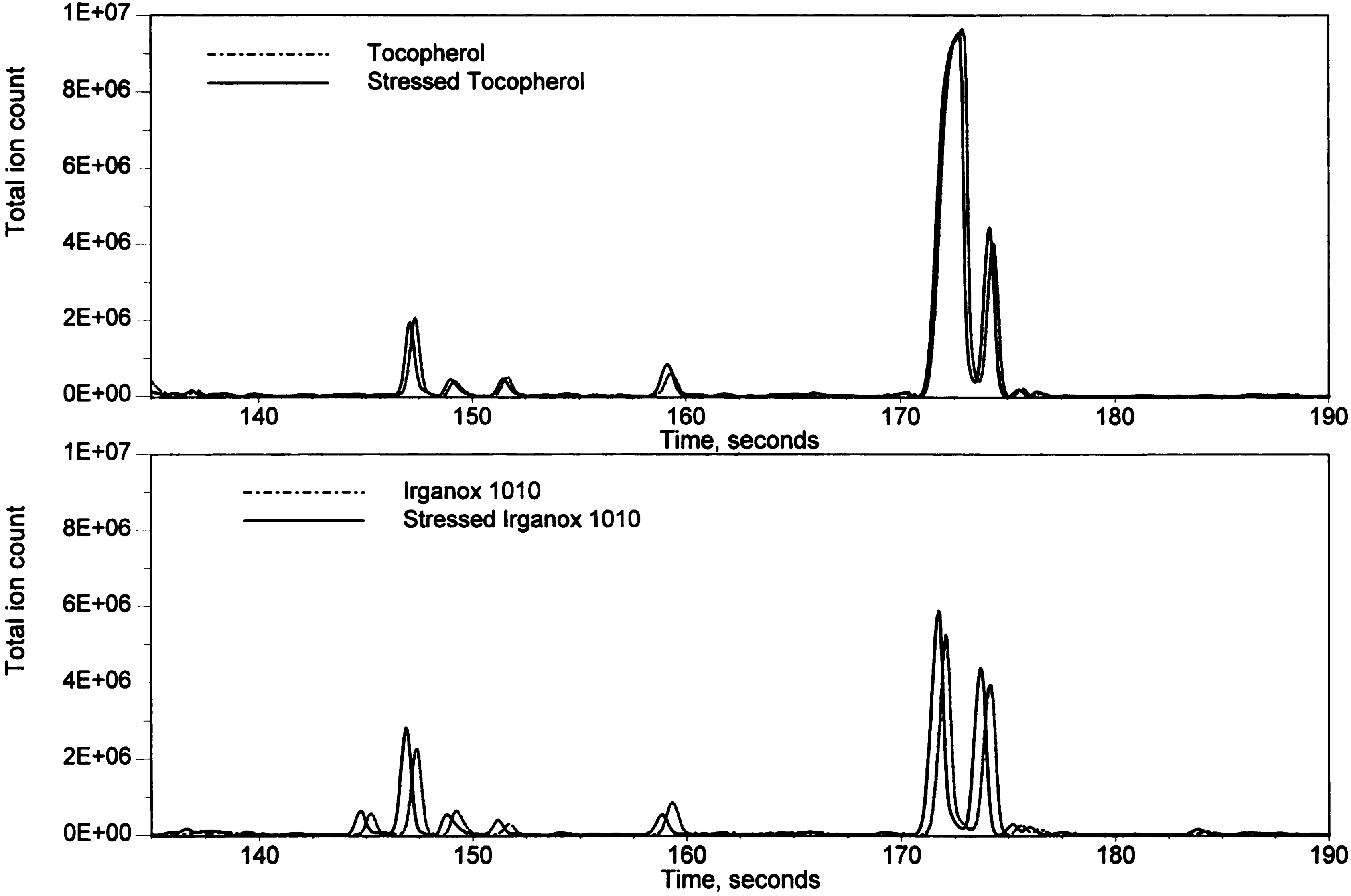


Figure 31(a) Total chromatogram of four HDPE samples (135-190 sec.)

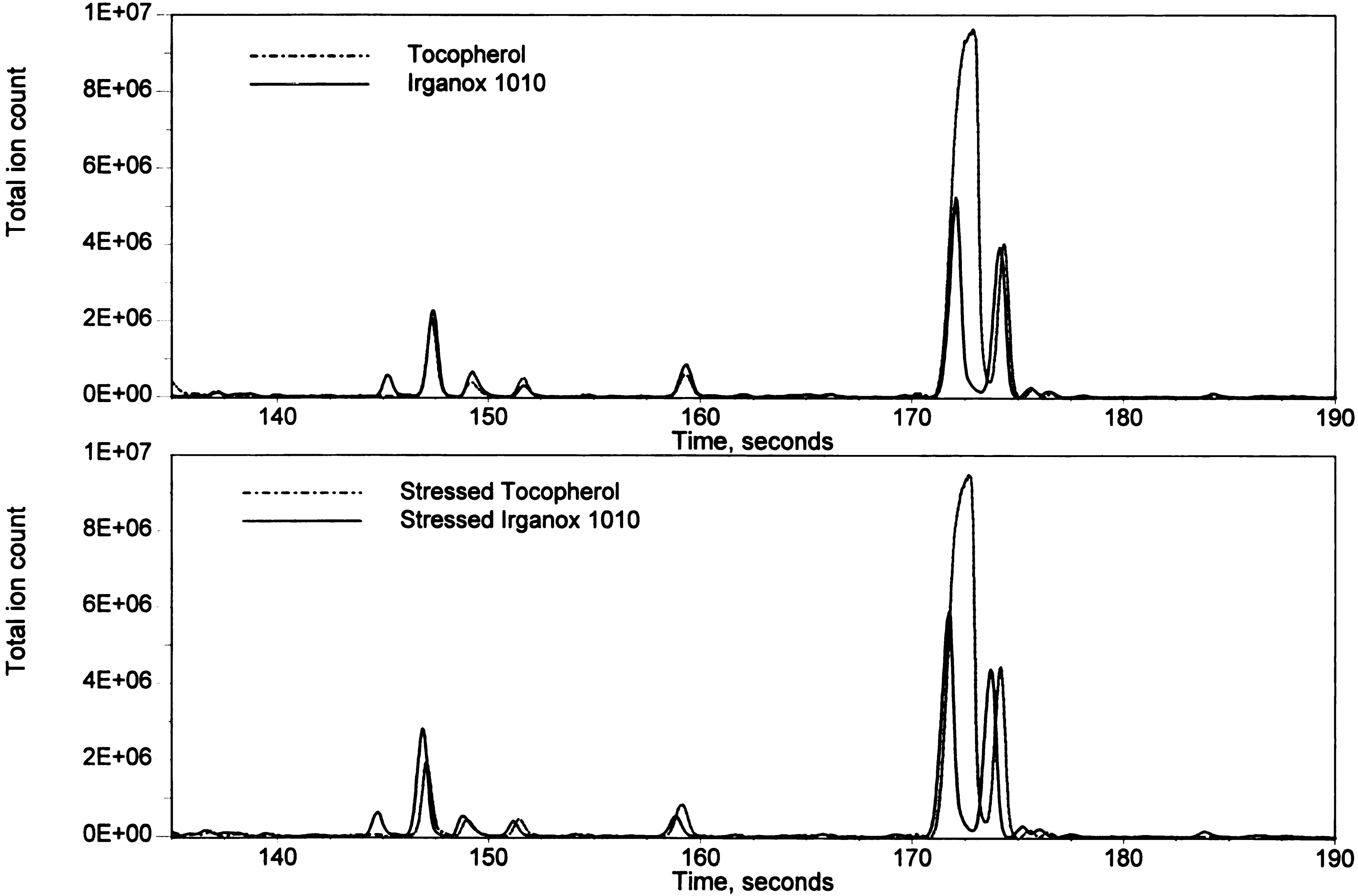


Figure 31(b) Total chromatogram of four HDPE samples (135-190 sec.)

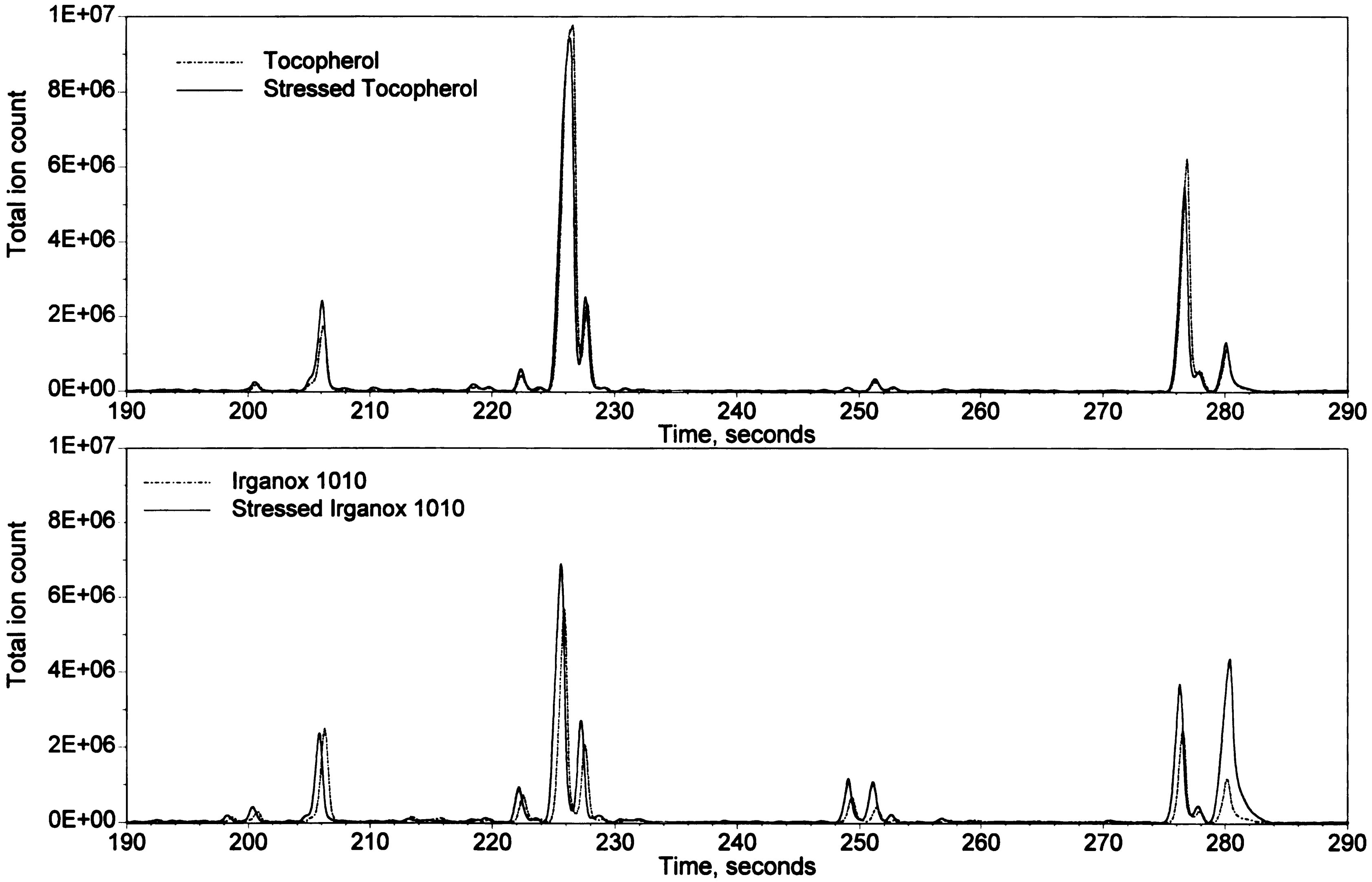


Figure 32(a) Total chromatogram of four HDPE samples (190-290 sec.)

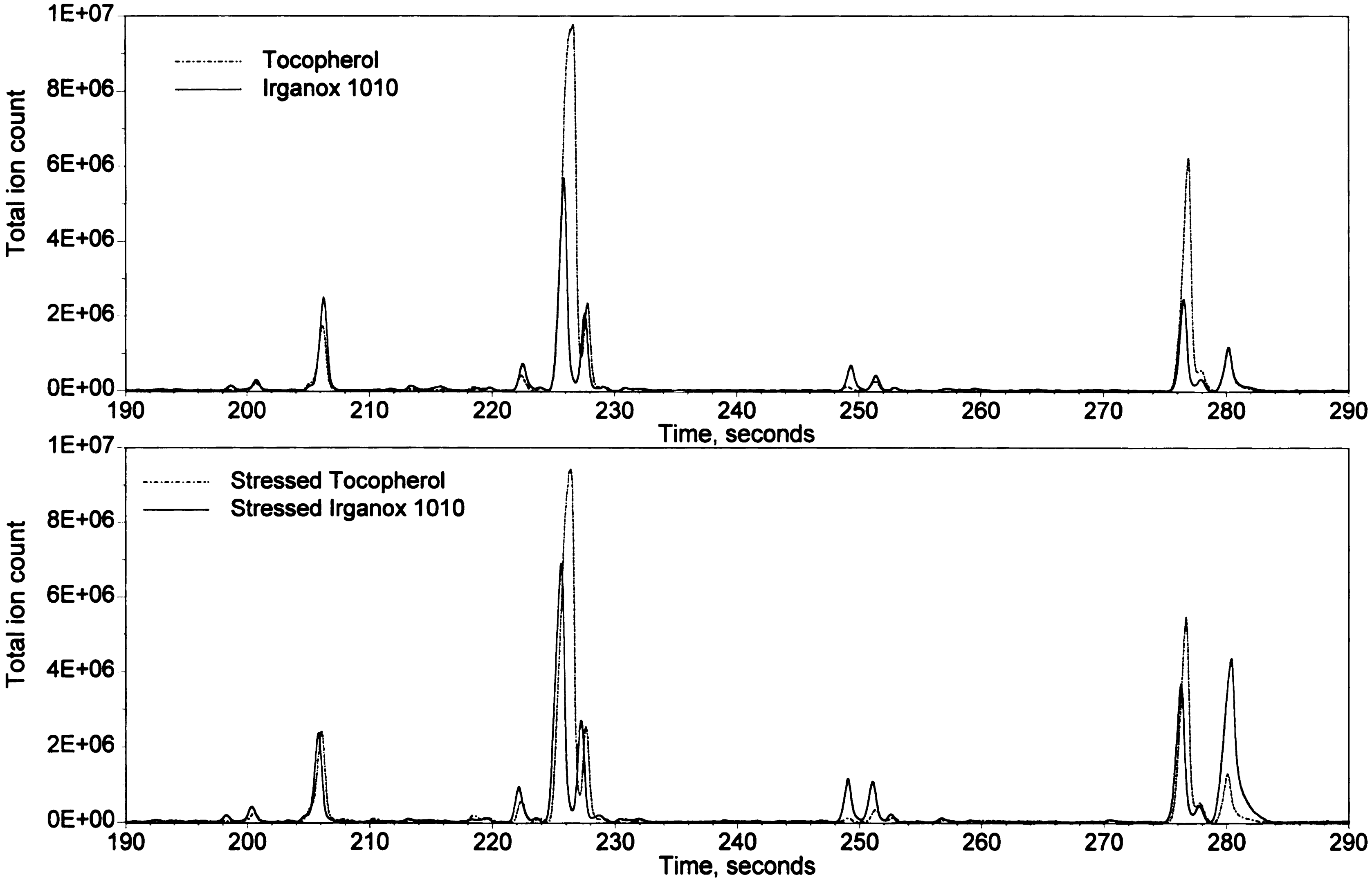


Figure 32(b) Total chromatogram of four HDPE samples (190-290 sec.)

There were slight differences in the total ion counts from the containers produced under normal and abusive temperature conditions. The correlation between the total ion counts and the fabrication temperatures was not conclusive. For example, higher total ion counts were found in the stressed Irganox 1010 sample than in the Irganox 1010 sample, except for a few compounds which eluted between 135-190 seconds. In contrast, all volatile compounds released from the α-Tocopherol sample had higher ion intensities or similar ion intensities to those released from the stressed α-Tocopherol sample, except 1-octene.

Comparisons between the total chromatograms from the HDPE samples produced using the same antioxidants are shown in Figure 29b, 30b, 31b and 32b. There were more volatile compounds found in the two α-Tocopherol samples than the two Irganox 1010 samples. For example, acetic acid and a C_9 olefin were identified in the α-Tocopherol sample, but not identified in the Irganox 1010 samples. Cyclopropane (76 sec.) and 1-tetradecene (225 sec.) were found in lower amounts in the two Irganox 1010 samples than in the two α-Tocopherol samples. A C_{11} olefin (142 sec.), 1-undecene (145 sec.) and 1-tridecene (197 sec.) were identified in the two Irganox 1010 samples, but not identified in the two α-Tocopherol samples. Nonane (134.5 sec.) was identified in the stressed α-Tocopherol sample, but was not identified in the stressed Irganox 1010 samples.

Total ion counts of the compounds released from the Irganox 1010 and stressed Irganox 1010 samples were similar or lower than the α-Tocopherol and stressed α-Tocopherol samples, respectively. However, 1-octene (100.5 sec) was found at a higher level in the Irganox 1010 sample than the α-Tocopherol sample, and there was a higher level of nonanal in the Irganox 1010 samples than the α-Tocopherol sample.

2.2. Quantification of a specific off-odor compound from HDPE containers using GC-MS analysis

The retention time of nonanal (GC-MS) was approximately 149 seconds. Nonanal was identified using the standard library of mass spectra (version 1.6d; National Institute of Standards and Technology). Nonanal was also correctly identified by peak comparison between the mass spectrum of the authentic compound and the unknown mass spectrum as shown in Figure 33.

As shown in Figure 33, mass 57 is one of the most abundant mass fragments in nonanal, and so it can be used to estimate the amount of nonanal in the volatile headspace of HDPE container samples. A standard calibration curve of nonanal was established as shown in Appendix D. Based on mass 57, peak area integration of nonanal in the HDPE samples was conducted and compared to the area responses with the standard calibration curve.

Table 8 presents the amount of nonanal in the four samples after container fabrication. There were 0.38, 0.32, 0.50 and 0.40 ppm of nonanal in α-Tocopherol, stressed α-Tocopherol, Irganox 1010 and stressed Irganox 1010 samples, respectively. Initially, after container fabrication, nonanal was found at higher levels in Irganox 1010 samples than α-Tocopherol samples. The stressed α-Tocopherol sample had the lowest level of nonanal, which was statistically different ($p<0.05$) from the stressed Irganox 1010 sample.

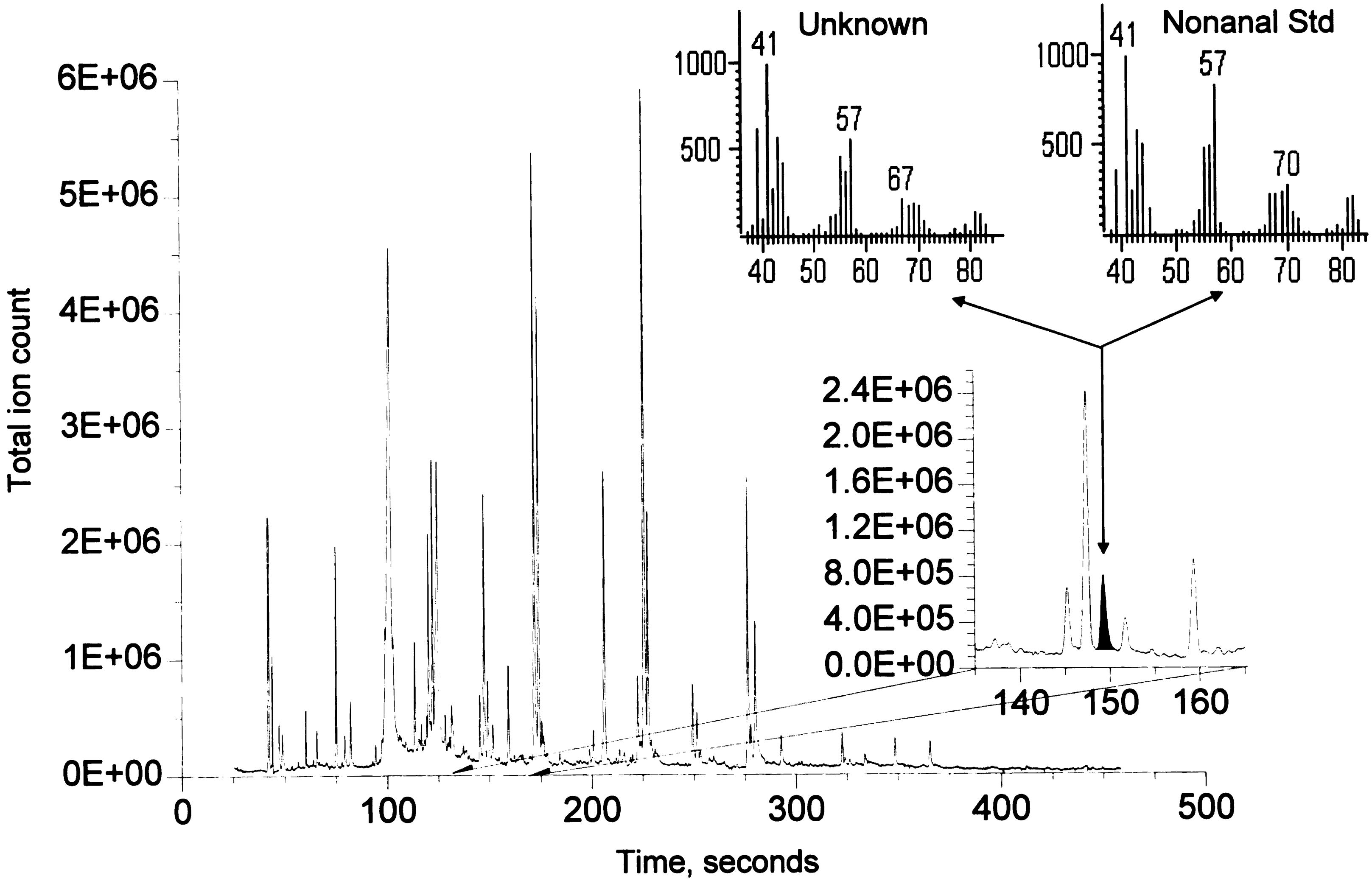


Figure 33 Identification of nonanal from HDPE sample

Table 8 Nonanal levels in four HDPE samples following fabrication

Treatment	Nonanal (ppm)
α-Tocopherol	0.38 ± 0.07^{ab}
Stressed α-Tocopherol	0.32 ± 0.02^{a}
Irganox 1010	0.50 ± 0.11^{b}
Stressed Irganox 1010	0.40 ± 0.10^{ab}

Note: The same letter (a, b) in the same column indicates no significant difference ($p>0.05$)

There was a lower amount of nonanal in the container samples produced with α-Tocopherol as antioxidant than the containers produced using Irganox 1010. α-Tocopherol performed better than Irganox 1010 in preventing the formation of nonanal during container fabrication. These results are in agreement with the findings of Ho et al. (1994) and Yam et al. (1996) who found that HDPE bottles containing vitamin E (α-Tocopherol) released the least amounts of aldehydes and ketones in comparison to HDPE bottles containing BHT and Irganox 1010.

Although it was not statistically significant ($p<0.05$), containers produced at higher temperature had lower levels of nonanal than the containers produced at low temperature. At higher temperature, nonanal may evaporate from the polymer matrix during container fabrication. In addition, nonanal may break down into oxidative precursors, which can react further to reform nonanal or other volatile components. Figure 34 shows the increase in nonanal levels during a three days evaluation period. An increase in nonanal after three days may have been due to transformation of oxidative precursors into nonanal during storage (Van Leeuwen, 1997).

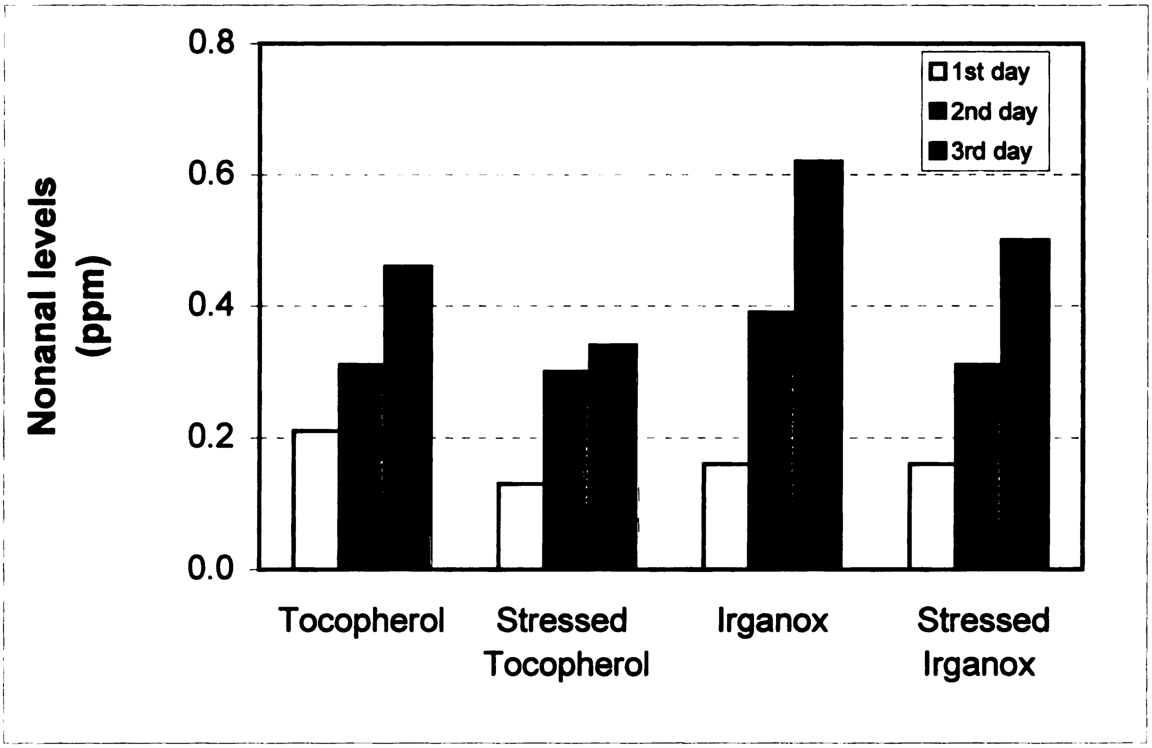


Figure 34 Nonanal levels in HDPE samples (three days GC-MS analysis)

3. Determination of the extent of the off-odor compounds released from HDPE containers using GC-MS, electronic nose and sensory analysis

3.1. Odor analysis of water samples using the electronic nose system

Volatile compounds such as nonanal can transfer into water during storage (Linssen et al., 1991; Ho et al., 1994; Yam et al., 1996 and Van Leeuwen, 1996). Volatile compounds can be present in very low levels and still cause off-odor or off-taste problems. Water samples were subjected to electronic nose evaluation, and PCA was conducted to determine the difference between water samples packaged in glass and HDPE containers.

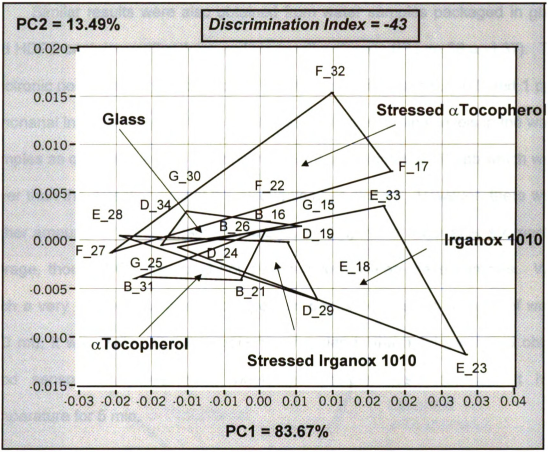


Figure 35 PCA of water samples stored in HDPE containers for 24 hours

PCA mapping of water packaged in glass and HDPE containers prior to storage is shown in Figure 35. There was overlap between the water samples packaged in the four HDPE containers and the glass container. The electronic nose technique with principal components analysis could not discriminate between the water stored in the HDPE containers and the glass container at 24 hours. Thus, transfer of the volatile compounds prior to storage (24 hours) was below the sensitivity limit of the electronic nose system. The initial concentration of nonanal as determined by GC-MS analysis was 12.6 ppb, but the sensitivity of the electronic nose system was 0.1 ppm.

Similar results were also obtained from water samples packaged in glass and HDPE containers after three and six months storage (Figure 36 and 37). The electronic nose system was capable of discriminating between 0.1, 0.5 and 1 ppm of nonanal in triacetin. After three months storage, the nonanal levels in the water samples as quantified by GC-MS analysis, were approximately 50 ppb which were lower than the detection limit of the electronic nose system. However, there were higher amounts of nonanal (approximately 0.2 ppm) in the water after six months storage, though PCA still could not discriminate between these samples. With such a very low level of volatile compounds present in a small amount of water (3.0 ml), it was quite difficult to generate volatiles in the headspace and obtain good sensor responses, even when the sample was incubated at high temperature for 5 min.

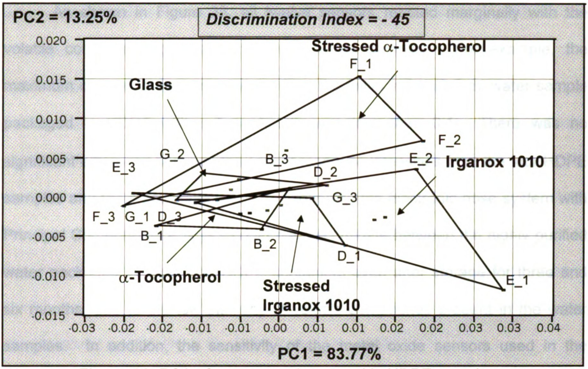


Figure 36 PCA of water samples stored in HDPE containers stored at 38°C, 65%RH for 3 months

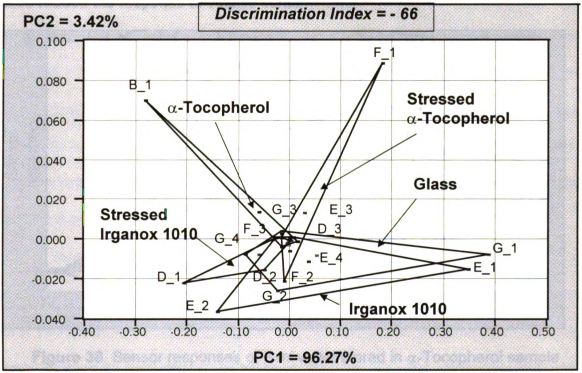


Figure 37 PCA of water samples stored in HDPE containers stored at 38°C, 65%RH for 6 months

As shown in Figure 38, all twelve sensors reacted marginally with the volatile compounds generated from the water samples. For example, the maximum change in sensor response from the initial value (3.0 ml water sample packaged in HDPE with α-Tocopherol), was less than 0.1. There was no significant difference between the sensor response intensities from the four HDPE samples and the glass container. Consequently, the electronic nose system with Principal Components Analysis could not discriminate between the highly purified water packaged in glass and HDPE containers even after storage for three and six months, due to the low intensity of volatile compounds present in the water samples. In addition, the sensitivity of the metal oxide sensors used in the electronic nose system is affected by relative humidity (Mielle, 1996). This may also reduce the response to volatile contaminants.

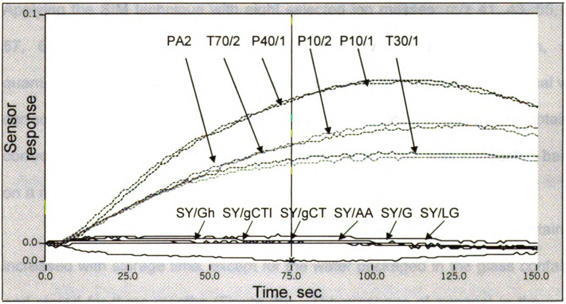


Figure 38 Sensor responses of 3 ml water stored in α-Tocopherol sample for six months

3.2. Identification and quantification of specific off-odor compounds in the water samples using GC-MS analysis

Using thermal desorption with GC-MS analysis, saturated aldehydes and ketones ranging from C_5-C_{11} were identified in HDPE samples containing different resin-antioxidant formulations (Yam et al, 1996). Although several aldehydes, i.e. pentanal, hexanal, decanal, undecanal and benzaldehyde were detected, their levels were considerably low probably due to their greater tendency to escape to the gas phase during the blow-molding process. Nonanal is likely a major contributor to container off-odor because of its abundance, low odor threshold and low molecular weight (Ho et al., 1994; Yam et al., 1996).

Thermal stripper/thermal desorption with GC-MS analysis was used to identify and quantify nonanal in water packaged in glass and HDPE containers. Applying the SIM technique with eight selected ion masses; m/z 41, 43, 55, 56, 57, 60, 70, 98, increased the system sensitivity; thus identification, and quantification of nonanal in the water samples could be carried out. Nonanal was correctly identified by direct injection of authentic standard nonanal, to obtain a correct retention time. Quantification of nonanal in water was conducted based on a nonanal standard calibration curve (Appendix E).

Nonanal concentration in water packaged in glass and HDPE containers increased with storage time, except for the water packaged in the glass container and stored for three months (Figure 39). The presence of nonanal in the water may be due to migration or transfer of nonanal from the container into water during container fabrication (Van Leeuwen, 1997). In addition, a secondary degradation process also occurs during storage. It is possible that intermediates or redicals, i.e. hydroperoxides, still present, reacted further generating a new radical and/or nonanal.

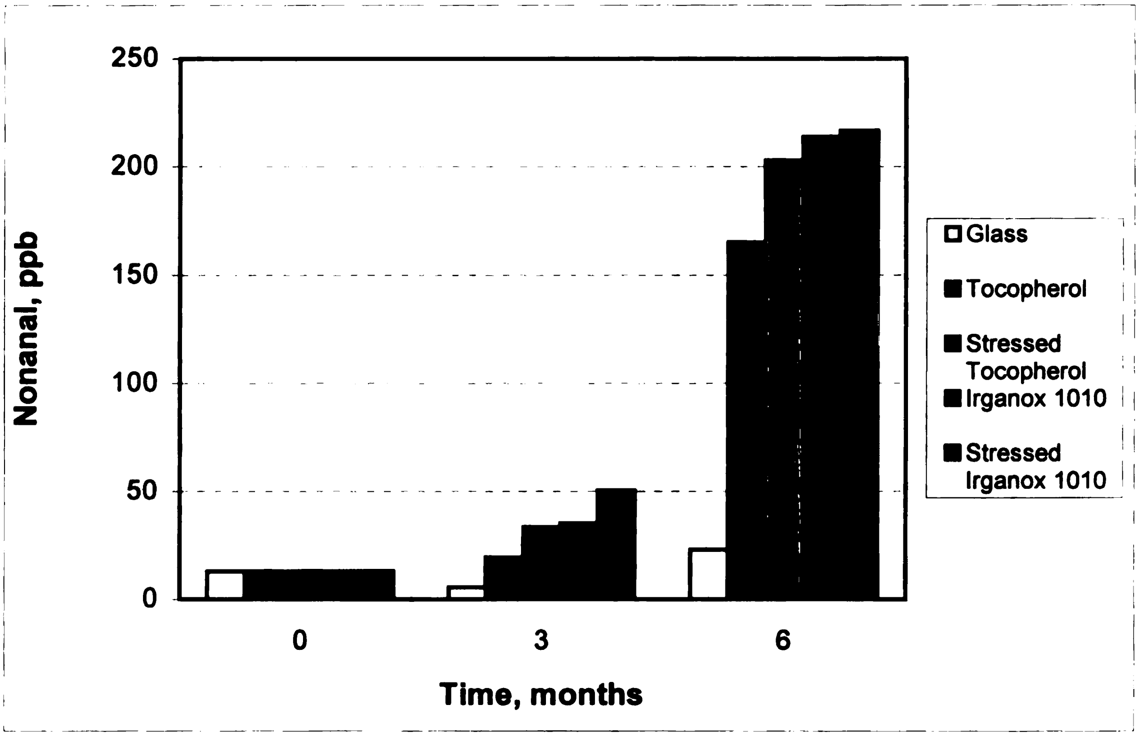


Figure 39 Nonanal levels in water obtained from the four HDPE samples after storage

After three months storage, there were significant increases in nonanal levels in water from the four HDPE containers (Table 9). Nonanal levels in water packaged in α-Tocopherol, stressed α-Tocopherol, Irganox 1010 and stressed Irganox 1010 samples were 19.5, 33.6, 35.3 and 50.3 ppb, respectively. The lowest nonanal level (19.5 ppb) was found in the water packaged in HDPE bottles containing α-Tocopherol, while the water packaged in HDPE bottles containing Irganox 1010, and produced at high temperature had the highest nonanal level (50.3 ppb). There was a significant difference ($p<0.05$) between nonanal concentrations in water obtained from α-Tocopherol samples and stressed α-Tocopherol, Irganox 1010 and stressed Irganox 1010, but there was no significant difference between nonanal concentrations in water from the stressed α-Tocopherol and Irganox 1010 samples.

Table 9 Nonanal concentrations (ppb) in water packaged in glass and HDPE containers

Container/Storage time	Initial	3 months	6 months
Glass	12.9 ± 2.2	5.5 ± 0.3[a]	23.0 ± 9.8[a]
α-Tocopherol	12.9 ± 2.2	19.5 ±0.1 [b]	165.1 ±16 [b]
Stressed α-Tocopherol	12.9 ± 2.2	33.6 ±1.0[c]	202.9 ± 8.1[c]
Irganox 1010	12.9 ± 2.2	35.3 ± 3.3[c]	213.7 ± 1.8[c]
Stressed Irganox 1010	12.9 ± 2.2	50.3 ± 8.6[d]	216.4 ± 8.9[c]

Note: The same letter (a, b, c, d) in the same column indicates no significant difference ($p>0.05$)

Following fabrication of the containers, nonanal was present as follows, stressed α-Tocopherol< α-Tocopherol = stressed Irganox 1010 < Irganox 1010 samples (Table 8). However, relative levels of nonanal in the water samples packaged in the four HDPE containers after storage were as follows; α-Tocopherol< stressed α-Tocopherol< Irganox 1010< stressed Irganox 1010 samples. This follows the earlier explanation by Van Leeuwen (1997) that not only can nonanal migrate from the container, but additional generation of nonanal can occur during storage. Moreover, it indicates that nonanal can be formed and transferred from containers produced at high temperature, even when the initial nonanal levels are low. Thus, containers produced using abusive conditions probably contain a great number of intermediate precursors that can lead to other volatile compounds.

There were large increases of nonanal in the water packaged in the four HDPE containers after six months storage. The lowest nonanal level (165.1 ppb) was found in water packaged in bottles containing α-Tocopherol and produced at a normal temperature condition. This was significantly different from the water samples packaged in the other HDPE containers. Higher initial nonanal level in the water was predictive of further generation of nonanal during storage.

There was no significant difference ($p>0.05$) between nonanal levels in stressed α-Tocopherol and Irganox 1010 samples and between stressed α-Tocopherol, Irganox 1010 and stressed Irganox 1010 after three and six months, respectively. There were substantial numbers of intermediate compounds in the polymer matrix that could further react to form additional volatile compounds. Thus, using α-Tocopherol as an antioxidant did not prevent the generation of intermediate compounds in the polymer matrix when containers were fabricated at abusive temperature.

A small increase of nonanal in water packaged in the glass container after six month storage may be due to oxidative break down of organic substances in the water (Ho et al., 1994). However, nonanal was present in significantly lower levels in water in the glass container than in the four HDPE containers. A small increase of nonanal level after six months may be due to system contamination, which was not significantly different to the initial concentration. This indicates that nonanal mainly migrated from the HDPE container surfaces into the water.

3.3. Sensory evaluation

Figure 40 presents the average sensory scores of water packaged in four HDPE containers after three and six months storage at 38°± 2°C. The higher the sensory score, the more unacceptable is the water as compared to the reference sample (water in glass container).

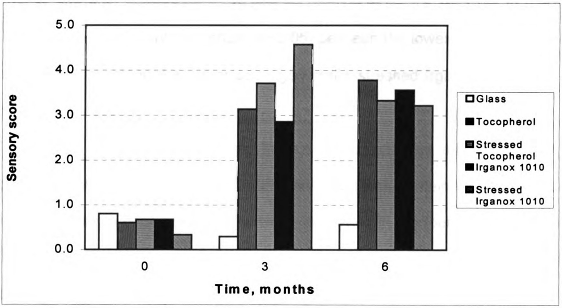


Figure 40 Sensory scores of water packaged in glass and HDPE containers

Initially, water was evaluated from the respective HDPE containers after 24 hours storage. The odor scores were very low indicating that the water was still acceptable to the panelists. There was no significant difference between the water packaged in glass and HDPE containers.

There was evidence of volatile compounds from the HDPE containers transferring to the water samples after three and six months storage at 38±2°C. Panelists were able to detect the odor differences between the four HDPE containers and the glass container. An increase in sensory score after storage indicated transfer of off-odor compounds, i.e. aldehydes and ketones, from HDPE containers into the water. For example, after three and six months storage, nonanal was found in higher amounts in the water packaged in the four HDPE containers compared to the water in the glass container. Table 10 presents the average sensory scores of water packaged in glass and four HDPE containers prior to and after storage for three and six months at 38 ± 2°C. Prior to storage, there was no significant difference ($p > 0.05$) between the lowest and highest odor scores, obtained from the water packaged in the stressed Irganox 1010 and the glass containers.

After three months storage, there was a significant difference ($p<0.05$) between water stored in the four HDPE and the glass containers. There was a large increase in odor scores of the water packaged in the four HDPE containers compared to the reference sample. Water packaged in the Irganox 1010 and stressed Irganox 1010 containers had the lowest (2.86) and highest (4.57) sensory scores, respectively. However, there was no significant difference

($p>0.05$) between the water packaged in the Irganox 1010, α-Tocopherol and the stressed α-Tocopherol containers. Water samples from the container with Irganox 1010 fabricated at high temperature had the highest off odor intensity, which was statistically significantly different ($p< 0.05$) from the water samples from the HDEP containers produced at normal temperature conditions using either Irganox 1010 or α-Tocopherol as antioxidants.

Table 10 Sensory scores of water samples packed in HDPE containers

Sample	Initial	3 months	6 months
Glass container	0.80 ± 0.71^{a}	0.29 ± 0.49^{a}	0.56 ± 1.01^{a}
α-Tocopherol	0.60 ± 0.47^{a}	3.14 ± 1.21^{b}	3.78 ± 1.09^{b}
Stressed α-Tocopherol	0.67 ± 0.72^{a}	3.71 ± 1.11^{bc}	3.33 ± 0.87^{b}
Irganox 1010	0.67 ± 0.72^{a}	2.86 ± 1.21^{b}	3.56 ± 0.89^{b}
Stressed Irganox 1010	0.33 ± 0.45^{a}	4.57 ± 0.53^{c}	3.22 ± 1.40^{b}

Note: The same letter (a, b, c) in the same column indicates no significant difference ($p>0.05$)

After six months storage, there was a small increase in sensory scores for all water samples, except for the water packaged in the HDPE container with Irganox 1010 and fabricated at high temperature. There was no significant difference ($p>0.05$) between the water packaged in the four HDPE containers.

The off-odor may have been so severe that the panelists could not detect any difference between the samples.

Antioxidant type and processing conditions can affect the formation of volatiles contributing to off flavor. Antioxidants such as α-Tocopherol reduce the development of off flavors from HDPE containers during processing (Ho et al., 1994; Yam et al., 1996). The difference in sensory scores between the water packaged in containers fabricated at normal and abusive temperature conditions indicates that the temperature showed more effect on the odor scores of water samples, when Irganox 1010 was used.

Al-Malaika and Issenhuth (1999) investigated the effect of processing severity on the nature and amount of transformation products formed during polyolefin extrusion. The authors found that stereoisomers of the oxidative products, i.e. dihydroxydimers (DHD), spirodimers (SPD), trimers (TRI), and aldehydes are formed during extrusion of LDPE stabilized with α-Tocopherol. The effect of temperature on the amount of transformation products was studied using PP, which is more sensitive to oxidation than PE (Hinsken et al., 1991). For PP containing 300 ppm of α-Tocopherol and an extrusion temperature of 290°C, there was a significant increase in the concentration of several intermediates as well as an absence of other intermediates, due to loss of the antioxidant. If the temperature was lower than 275°C, temperature had little effect on the concentration levels of the transformation products. This supports the results that showed no significant difference between the odor scores of α-Tocopherol and stressed α-Tocopherol since both container samples were produced at a temperature lower than 275°C.

The higher sensory scores were not always obtained from the water samples with the higher nonanal concentrations. For example, the water packaged in α-Tocopherol containers produced at normal temperature had the lowest nonanal level, but the sensory score was higher than that obtained from the Irganox 1010 container. While nonanal was present in a lower amount, other volatile compounds, i.e. aldehydes and ketones could present in higher levels and cause an off-odor problem. Off-odor from HDPE containers may result from either a single volatile compound or a combination of several volatile compounds (Koszinowski and Piringer, 1986; Linssen et al., 1996; Van Leeuwen et al., 1997). It is also possible that the total concentration of aldehydes and ketones determines the off-flavor from HDPE containers (Van Leeuwen et al., 1997; Yam et al., 1997).

4. Determination of the oxidation levels of the HDPE surfaces using surface analysis techniques

4.1. Determination of the oxidation levels of the HDPE surfaces using Fourier Transform-Infrared (FT-IR) spectroscopy

The infrared spectra obtained from the four HDPE samples prior to and after three and six months storage are shown in Appendix F. The four spectra seem to be identical, and illustrate the absorption properties of polyethylene.

However, the FT-IR shows only very weak absorption bands in the carbonyl region.

The oxidation index of the container surface can be used as an indication of the amount of oxidative degradation. The β-scission of the alkoxy radical and the breakdown of the peroxy radical will yield aldehydes and ketones (Hinsken et al., 1991). Generally, the oxidation state of polyolefin is indicated by the relative levels of carbonyl groups contained (Kuijk and Warnar, 1993). Thus, the oxidation index is calculated using the ratio of the absorption values at 1720 cm^{-1} and 2720 cm^{-1}, representing the carbonyl and allyl groups, respectively.

Table 11 shows the oxidation indices obtained from the four HDPE container surfaces. After fabrication, stressed α-Tocopherol had a higher oxidation level than α-Tocopherol, while stressed Irganox 1010 had a slightly higher oxidation level than Irganox 1010. Kuijk and Warnar (1993) reported that the oxidation index of cast LDPE film increased exponentially with extrusion temperature. However, in this research, the differences found were not statistically significant, even HDPE containers produced at the higher temperature had higher oxidation levels than the containers produced at normal processing conditions.

After three and six months storage, the oxidation indices tend to decrease except those for stressed α-Tocopherol and Irganox 1010 after six months storage. A decrease in oxidation level may be due to leaching or migration of carbonyl compounds into the water from the package. Carbonyl compounds tend to easily transfer into the water, due to their polarity (Linssen et al., 1991; Van Leeuwen et al., 1997).

Table 11 Oxidation indices of four HDPE container surfaces

Sample	Initial	3 months	6 months
α-Tocopherol	0.38 ± 0.06^{a}	0.27 ± 0.04^{ab}	0.20 ± 0.04^{a}
Stressed α-Tocopherol	0.44 ± 0.15^{a}	0.15 ± 0.03^{a}	0.20 ± 0.01^{a}
Irganox 1010	0.33 ± 0.01^{a}	0.22 ± 0.01^{ab}	0.34 ± 0.03^{b}
Stressed Irganox 1010	0.34 ± 0.07^{a}	0.31 ± 0.15^{b}	0.22 ± 0.03^{a}

Note: The same letter (a, b) in the same column indicates no significant difference (p>0.05)

After three months storage, the oxidation indices decreased since polar compounds such as aldehydes may migrate from the container surface into water. In addition, the stressed Irganox 1010 sample had the highest oxidation index, which was significantly different from the stressed α-Tocopherol sample. This indicates that there were higher levels of aldehydes and/or ketones on the container surface, which could easily migrate into the water. Sensory evaluation also shows that the water packaged in this container had the highest unacceptable score.

Similarly, the levels of carbonyl compounds decreased after six months storage, except for the Irganox 1010 sample. The oxidation indices were lower than those values obtained from the containers after fabrication. This indicates leaching of some polar compounds after packaging. An increase in the oxidation index on the surface of Irganox 1010 containers resulted from the lower absorption value at 2720 cm^{-1}, which may occur due to surface contamination, as well as surface variation in surface characteristics from one container to another.

Surface analysis using FT-IR analysis and the oxidation index provides a better understanding of the container surface chemistry, particularly, following container fabrication. Other surface analysis techniques, such as ESCA, can provide additional information on the container surface chemistry.

4.2. Atomic oxygen concentrations using Electron Spectroscopy for Chemical Analysis (ESCA) measurement

The atomic oxygen concentration levels on the inner surface of the four HDPE samples are shown in Table 12. ESCA was performed in duplicate, so no statistical analysis was performed.

Table 12 Atomic oxygen concentration on the inside surface of HDPE container samples as evaluated using ESCA

Sample	Initial	3 months	6 months
α-Tocopherol	0.9	3.8	6.9
Stressed α-Tocopherol	1.0	8.2	4.3
Irganox 1010	0.5	7.0	3.1
Stressed Irganox 1010	0.7	4.9	3.9

The atomic oxygen level on the surface is an indication of the oxidation occurring during processing and storage (Van Leeuwen et al., 1997). As shown, there were low levels of atomic oxygen on the surface of the four containers prior to storage. There was no significant difference between the oxygen levels found on the surfaces of the four containers. Thus, the oxidation levels were similar for the four containers, since the two antioxidants helped prevent oxidation during container fabrication.

There was an increase in the atomic oxygen level on the container surfaces after three and six months storage as shown in Table 12. After three months, the lowest and the highest values were obtained from α-Tocopherol and stressed α-Tocopherol samples, respectively. Irganox 1010 and α-Tocopherol had the lowest and highest oxygen values after six months storage. However, the oxygen levels were of the same magnitude since both antioxidants helped to prevent surface oxidation during storage.

While this is not fully understood, it may be due to volatile compounds migrating to the container surface from the polymer bulk phase, and also surface oxidation may have occurred during storage. Van Leeuwen et al. (1997) suggested that oxygen levels increase after storage due to the transfer of degradation products from the polymer matrix to the container surface. The author also suggested that antioxidants such as α-Tocopherol help to prevent further oxidative degradation of the intermediate compounds during storage, thus oxygen levels decrease.

5. Correlations between electronic nose sensor responses, GC-MS and sensory analysis

5.1. Electronic nose sensor responses vs. GC-MS analysis

5.1.1. HDPE container samples

As shown in Figure 41, principal components analysis was used to discriminate between the four HDPE containers. Principal components analysis was also performed on the GC-MS data using the area response associated with mass 57 (m/z 57) and selected compounds found in the four samples. PCA mapping was compared to the results obtained from electronic nose analysis.

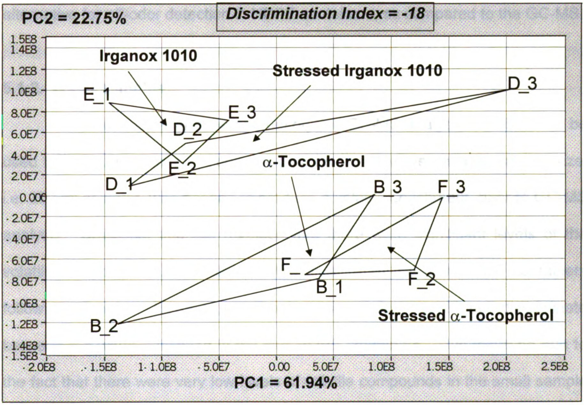


Figure 41 PCA mapping obtained from GC-MS area response of 9 specific odor compounds

Figure 41 presents PCA mapping of the area responses from nine selected compounds, which are believed to have significantly contributed to HDPE off-odor, particularly aldehydes, 1-alkenes and alkanes of dominant peaks. The selective compounds were hexane, cyclooctane, decane, dodecane, 1-decene, hexanal, nonanal, decanal, and undecanal. There was good separation between HDPE samples produced using the different antioxidants, which indicated that there were different combinations of odor contributors from these two groups of samples. The results also agreed with the electronic nose system sensor responses that found discrimination of volatiles from HDPE samples containing the different antioxidants. Thus, the electronic nose system offers a rapid alternative for off-odor detection in HDPE containers, as compared to the GC-MS.

5.1.2. Water samples

Thermal stripper and thermal desorption GC-MS analysis with SIM can be used to detect trace levels of nonanal (ppb level). However, a large sample size, i.e. 250 ml of water, was needed to produce a volatile enrichment, prior to GC-MS analysis. Statistical analysis revealed that there were significant levels of the volatile compounds, i.e. nonanal, in the water from the four HDPE containers following storage. However, electronic nose analysis could not discriminate between the water packaged in the four HDPE containers. This might be due to the fact that there were very low levels of volatile compounds in the small sample size (3 ml). It is difficult to generate the necessary volatiles because of the small headspace. Thus, special sample preparation techniques, i.e. Solid Phase Micro

Extraction (SPME), incorporated with the electronic nose system might prove to be useful. In addition, the high sensitivity of the metal oxide sensor to relative humidity may have affected the sensors.

5.2 Electronic nose sensor responses vs. sensory analysis

Due to low sensor responses, the electronic nose system was not capable of discriminating between the water samples packaged in HDPE containers after three and six months storage, as shown in Fig. 36 and 37. There was overlap between the water samples from HDPE and glass containers. Panelists, however, were able to indicate the difference between water packaged in HDPE containers after three months storage, based on the different antioxidants, and processing temperature (for Irganox 1010). The sensitivity of the sensory panels was much better than the instrumental methods.

5.3. GC-MS analysis vs. sensory analysis

After storage, there was evidence of transfer of volatile compounds from the HDPE containers into water as indicated by the GC-MS results. The volatile compounds absorbed and released by the bottle materials depend on several factors, including sorption characteristics of the volatile compounds in the polymer matrix, the thickness and surface area of the bottle and temperature (Ho and Yam, 1997). There were significant increases in nonanal levels after storage, as indicated by GC-MS analysis.

After three months storage, higher nonanal levels were found in the water packaged in the HDPE containers, especially in the Irganox 1010 sample produced at 204°C (400°F). This result agreed with the panelist results that the water sample packaged in this container had the highest unacceptable score. Statistical analysis ($p<0.05$) showed a significant difference between nonanal levels in water packaged in α-Tocopherol compared to Irganox 1010 container samples and stressed α-Tocopherol compared to stressed Irganox 1010 container samples after three months storage. On the other hand, panelists found a significant difference ($p< 0.05$) between water packaged in the stressed Irganox 1010 containers and the other containers. After six months storage, panelists could not detect the difference between water packaged in the four HDPE containers. There was a significant difference between the nonanal levels in water packaged in α-Tocopherol and the other container samples. It is difficult to develop a correlation between the amounts of nonanal transferring into water and the off-odor present in the water since the off-odor occurs due to a combination of total aldehyde and ketone compounds (Koszinowski and Piringer, 1986; Yam et al., 1996; Ho et al., 1997).

There were 12.9 ± 2.2 ppb of nonanal in the water prior to storage. Since the detection threshold of nonanal in water is 1 ng (Leffingwell and Leffingwell, 1991), the panelists should have been able to detect nonanal, but may not have recognized it as off-odor. Thus, the sensory scores were low and the water was rated as acceptable.

CONCLUSIONS

Based on PCA and PLS analysis, the twelve metal oxide sensors used in the electronic nose system were found to be able to differentiate between 0.1, 0.5 and 1 ppm dilutions of nonanal in triacetin (volume/volume) when incubated at 120°C for 15 min. However, the system was not capable of discriminating between 0.01, 0.1 and 0.5 ppm dilutions of nonanal in triacetin (volume/volume).

More than 40 volatile compounds were identified in the HDPE headspace, particularly, alkenes, alkanes, aldehydes, olefins and parrafins. There was a slight difference between the volatile compounds identified in HDPE containing α-Tocopherol and Irganox 1010, in terms of type of compounds and total ion intensity. Quantitative analysis also revealed that there was a lower amount of nonanal in the headspace of HDPE containers produced at 204°C (400°F) than 174°C (345°F).

Nonanal levels in water packaged in HDPE containers significantly increased after three and six months storage, indicating migration of volatile compounds from the HDPE containers into the water. The lowest nonanal level was found in water packaged in HDPE containing α-Tocopherol and produced at 174°C. This indicates that α-Tocopherol was more successful than Irganox 1010 in reducing the development of nonanal in the HDPE containers.

Neither FT-IR spectroscopy nor ESCA revealed any significant difference between the four container surfaces prior to and after storage.

There was good agreement between the electronic nose sensor responses and the GC-MS results in detection of volatiles from HDPE containers after fabrication. However, the correlation between the electronic nose sensor responses and sensory scores was not conclusive due to low electronic nose sensor responses.

APPENDICES

APPENDIX A

Table 13 Properties of nonanal and triacetin

Properties	Nonanal (Nonyl aldehyde)	Triacetin (1,2,3-Triacetylglycerol)
Formula	$CH_3(CH_2)_7CHO$	$C_9H_{14}O_6$
Density at 25°C	0.827 g/cm^3	1.155 g/cm^3
Molecular weight	142.24	218.2
Purity	95%	99%

Table 14 Properties of squalane

Formula	$[(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CH_2]_2$
Density at 25°C	0.810 g/cm^3
Molecular weight	422.83
Purity	99%

APPENDIX B

Sensory evaluation questionnaire

Sensory evaluation sheet for Semi-trained Panel

Name ______________________ Date 12/ 07/00

Type of sample Water

Instructions

1. Sniff and taste the sample marked 'Reference' first.
2. Sniff and taste the samples marked with the three digit codes from left to right.
3. Assess the overall sensory difference between the coded samples with the 'reference' using the scale below.
4. Distilled water will be served for oral rinsing between the samples.

0 = No difference
1 = Very slight difference
2 = Slight difference
3 = Moderate difference
4 = Large difference
5 = Extreme difference

Coded sample	**Sensory score / Degree of difference**
____	______________
____	______________
____	______________
____	______________
____	______________

REMEMBER THAT A DUPLICATE REFERENCE IS THE SAMPLE SOME OF THE TIME.

Comment:

APPENDIX C

Table 15 Volatile compounds released from HDPE samples identified by GC-MS analysis (Compound found in the samples if mark (/))

Compound	HDPE sample			
	α–Tocopherol	Stressed α–Tocopherol	Irganox 1010	Stressed Irganox 1010
Alkane				
Cyclopropane	/			
n-Heptane	/	/	/	/
n-Octane	/	/	/	/
n-Nonane	/	/		
n-Decane	/	/	/	/
n-Undecane	/	/	/	/
n-Dodecane	/	/	/	/
n-Tridecane	/	/	/	/
n-Tetradecane	/	/		
Alkene				
1-Heptene	/	/	/	
1-Octene	/	/	/	/
1-Nonene	/	/	/	/
1-Decene	/	/	/	/
1-Undecene			/	/
1-Dodecene		/	/	
1-Triedecene			/	/
1-Tetradecene	/	/	/	/
1-Hexadecene	/	/	/	/
Aldehyde				
Butanal	/		/	
Pentanal				/
Hexanal	/	/	/	/
Benzaldehyde	/	/	/	
Nonanal	/	/	/	/
2-nonenal			/	/
Decanal	/	/	/	/
Undecanal	/	/	/	/
Dodecanal	/	/	/	/
Ketone				
Methyl Isobutyl Ketone	/	/	/	/
2,2-Diemethyl, 3-Hexanone			/	

Table 15 (Con't)

Compound	HDPE sample			
	α–Tocopherol	Stressed α–Tocopherol	Irganox 1010	Stressed Irganox 1010
Olefin				
C-8		/	/	/
C-9	/	/		
C-10	/	/	/	/
C-11			/	/
C-12			/	/
C-13	/	/	/	/
C-14			/	/
C-15				/
C-16	/	/	/	/
Paraffin				
C-8	/	/	/	/
C-9	/	/		/
C-10	/	/	/	/
C-11		/		/
C-12	/		/	
C-13			/	/
C-15	/			
Other				
Acetic acid	/			
Ethanol-2-butoxy	/	/	/	/
Limonene	/	/	/	/
Phenol	/			

APPENDIX D

Identification and quantification of nonanal in HDPE samples

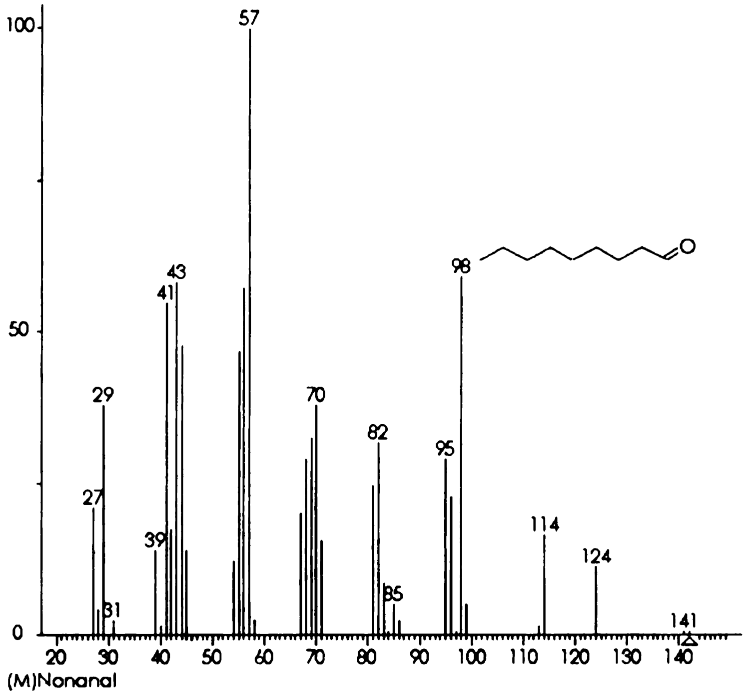


Figure 42 Chemical structure and ion mass spectra of nonanal (Nonyl aldehyde)

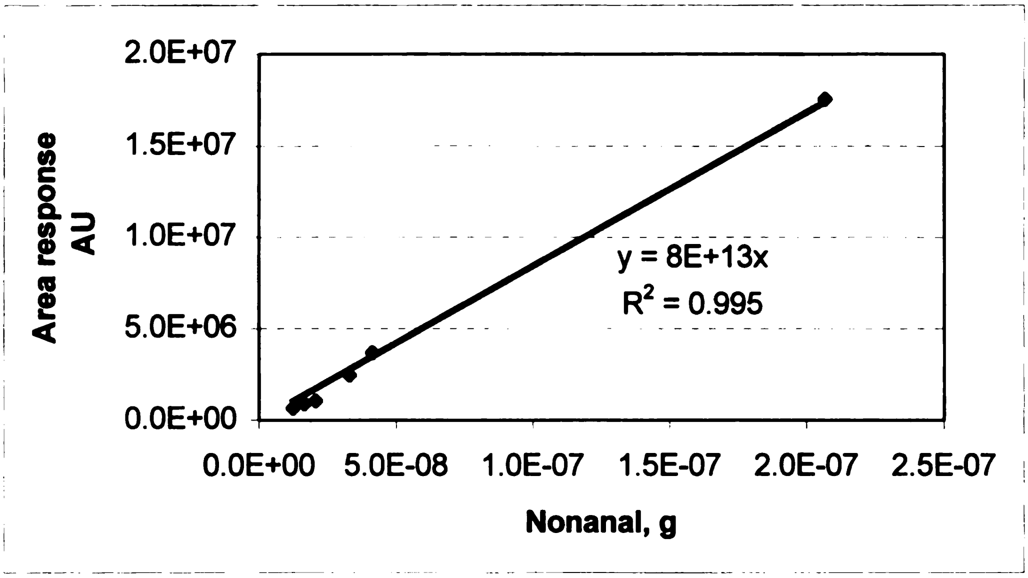


Figure 43 Nonanal standard curve for quantitative analysis of nonanal levels in four HDPE samples

APPENDIX E

Quantitative analysis of nonanal in water by GC-MS analysis: Nonanal standard curve

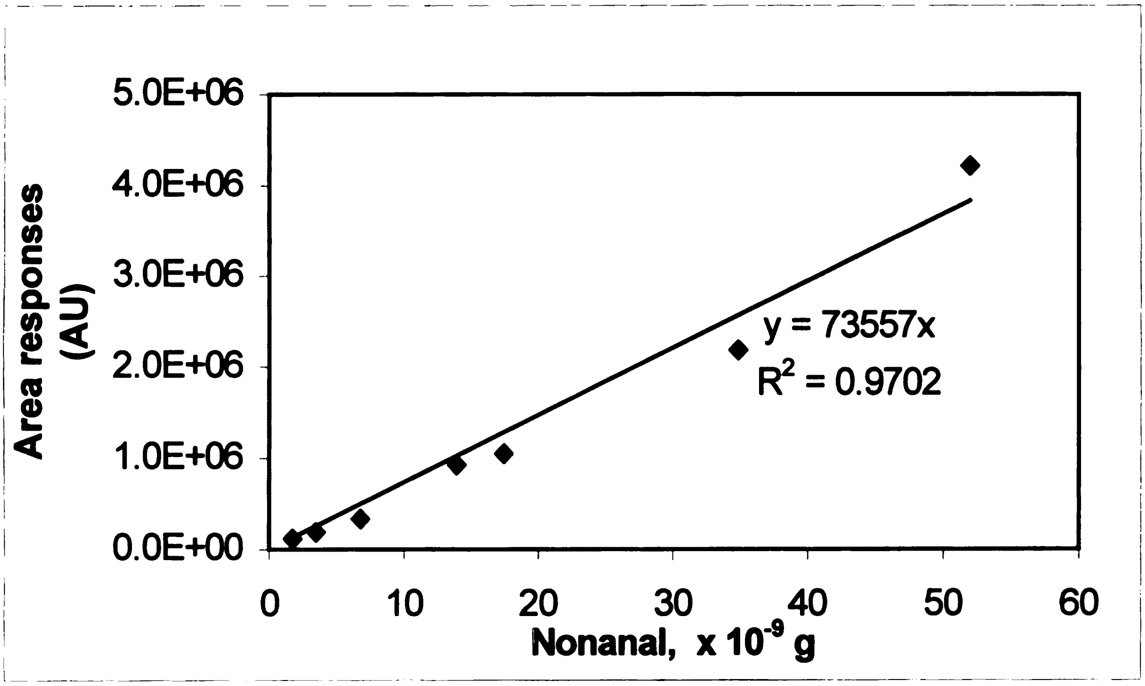


Figure 44 Nonanal standard curve for nonanal quantitative analysis of nonanal in water samples

APPENDIX F

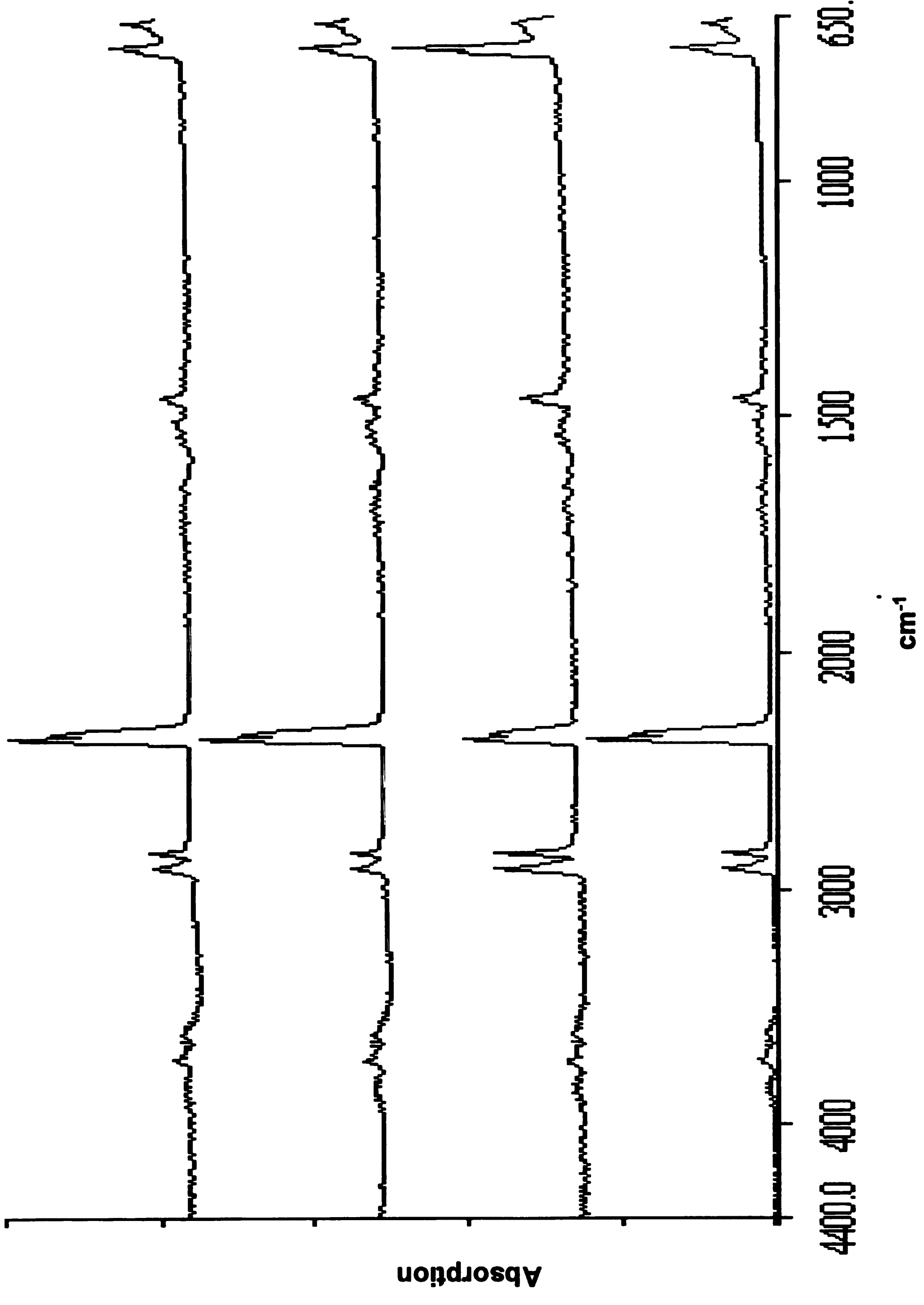


Figure 45 FT-IR spectra of four HDPE (Initial)

APPENDIX F

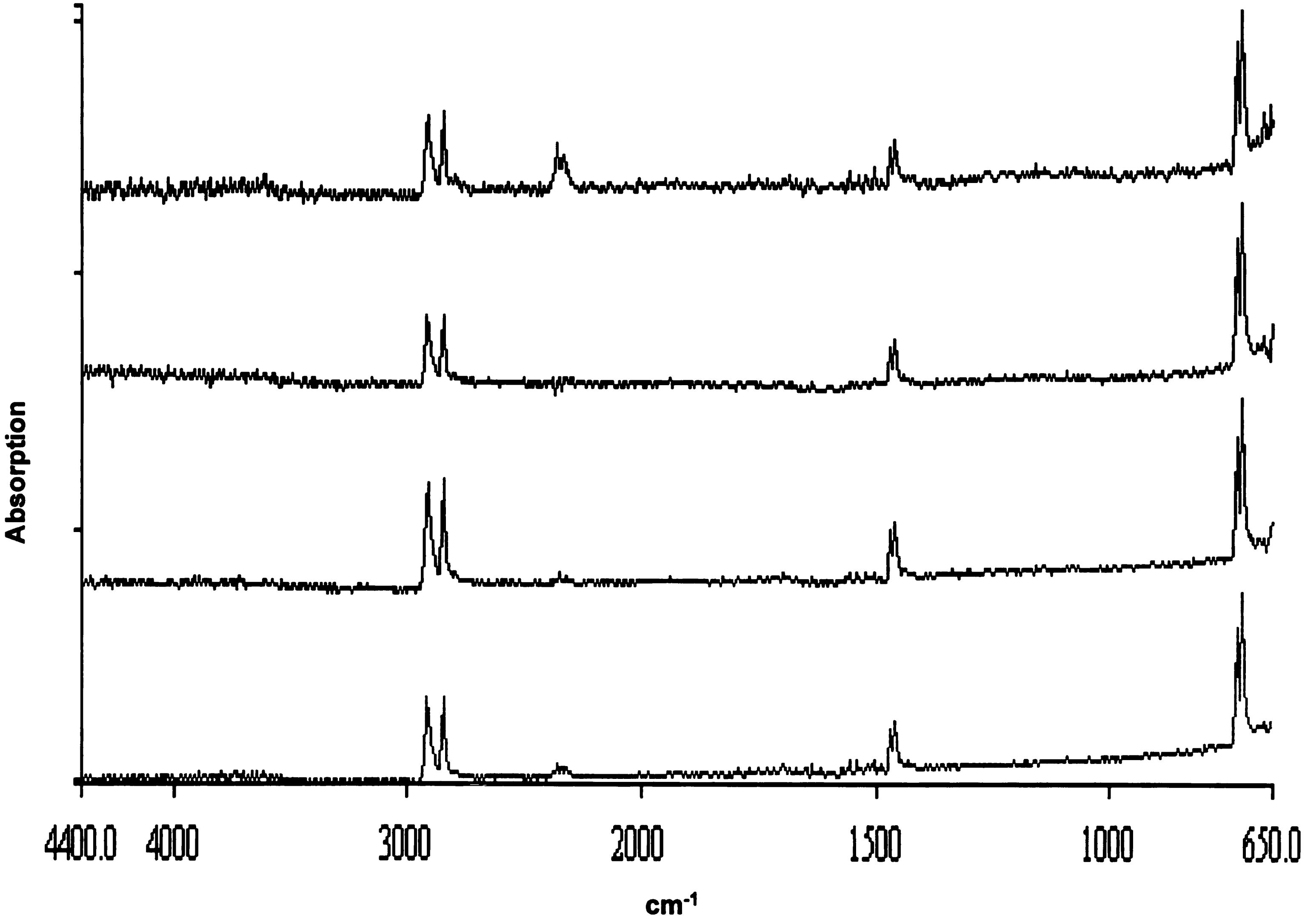


Figure 46 FT-IR spectra of four HDPE (3months)

APPENDIX F

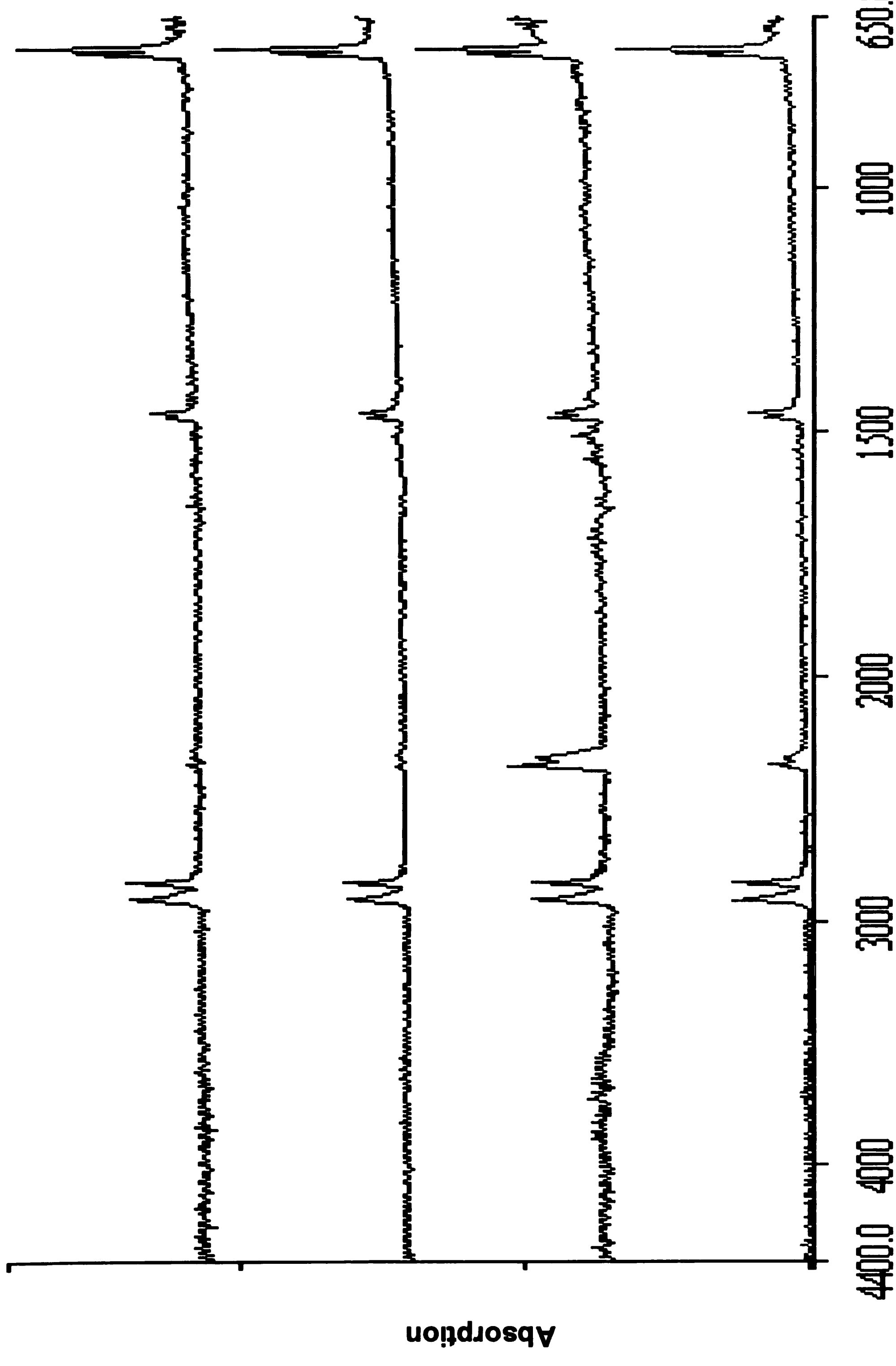


Figure 47 FT-IR spectra of four HDPE (6 months)

APPENDIX G

Statistical analysis: ANOVA Table and Duncan's New Multiple Range test

G-1. Nonanal levels in four HDPE samples

Table 16 ANOVA Table of nonanal levels in HDPE samples

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
NONANAL	Between Groups	5.105E-02	3	1.702E-02	2.434	.140
	Within Groups	5.592E-02	8	6.990E-03		
	Total	.107	11			

Table 17 Multiple comparisons between nonanal levels in HDPE samples

NONANAL

Duncan[a]

TREAT	N	Subset for alpha = .05	
		1	2
2	3	.3226	
1	3	.3826	.3826
4	3	.4028	.4028
3	3		.5037
Sig.		.292	.127

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 3.000

G.2. Nonanal levels in water packaged in HDPE and glass containers

G.2.1. After 3 months storage

Table 18 ANOVA Table of nonanal levels in water samples packaged in glass and HDPE containers – 3 months

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
THREE	Between Groups	462.632	4	865.658	50.194	.000
	Within Groups	172.463	10	17.246		
	Total	635.095	14			

Table 19 Multiple comparisons between water samples packaged in glass and HDPE containers – 3 months

THREE

Duncan[a]

		Subset for alpha = .05			
TREATMEN	N	1	2	3	4
1	3	5.5433			
2	3		19.5200		
3	3			33.5933	
4	3			35.2700	
5	3				50.3033
Sig.		1.000	1.000	.632	1.000

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 3.000

G.2.2. After 6 months storage

Table 20 ANOVA Table of nonanal levels in water packaged in HDPE and glass containers – 6 months

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
SIX	Between Groups	867.991	4	966.998	200.946	.000
	Within Groups	993.650	10	99.365		
	Total	861.642	14			

Table 21 Multiple comparisons between nonanal levels in water packaged in HDPE and glass containers – 6 months

SIX

Duncan [a]

TREATMEN	N	Subset for alpha = .05		
		1	2	3
1	3	22.9733		
3	3		165.1100	
2	3			202.9033
4	3			213.7000
5	3			216.4367
Sig.		1.000	1.000	.143

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 3.000

G.3. Sensory score of water packaged in glass and HDPE containers

G.3.1. Initial

Table 22 ANOVA Table of sensory scores-initial

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
INITIAL	Between Groups	1.668	4	.417	1.129	.351
	Within Groups	24.000	65	.369		
	Total	25.668	69			

Table 23 Multiple comparisons between sensory scores – initial

INITIAL

Duncan[a]

		Subset for alpha = .05
TREATMEN	N	1
5	14	.33
2	14	.60
3	14	.67
4	14	.67
1	14	.80
Sig.		.073

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 14.000

G.3.2. After 3 months storage

Table 24 ANOVA Table of sensory scores – 3 months

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
SEN3MO	Between Groups	72.457	4	18.114	19.212	.000
	Within Groups	28.286	30	.943		
	Total	100.743	34			

Table 25 Multiple comparisons between sensory scores – 3 months

SEN3MO

Duncan[a]

		Subset for alpha = .05		
TREATMEN	N	1	2	3
1	7	.29		
4	7		2.86	
2	7		3.14	
3	7		3.71	3.71
5	7			4.57
Sig.		1.000	.128	.109

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 7.000

G.3.3. After 6 months storage

Table 26 ANOVA Table of sensory scores – 6 months

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
SCORE	Between Groups	125.778	4	31.444	29.335	.000
	Within Groups	91.111	85	1.072		
	Total	216.889	89			

Table 27 Multiple comparisons between sensory scores – 6 months

SCORE

Duncan[a]

		Subset for alpha = .05	
TREATMEN	N	1	2
5	18	.56	
4	18		3.22
2	18		3.33
3	18		3.56
1	18		3.78
Sig.		1.000	.147

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 18.000

G.4. Oxidation indices of HDPE surfaces

G.4.1. Initial

Table 28 ANOVA Table of oxidation indices – initial

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
INITIAL	Between Groups	2.316E-02	3	7.719E-03	1.000	.441
	Within Groups	6.173E-02	8	7.717E-03		
	Total	8.489E-02	11			

Table 29 Multiple comparisons between oxidation indices – initial

INITIAL

Duncan[a]

TREATMEN	N	Subset for alpha = .05 1
3	3	.3300
4	3	.3433
1	3	.3800
2	3	.4433
Sig.		.176

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 3.000

G.4.2. After 3 months storage

Table 30 ANOVA Table of oxidation indices – 3 months

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
STORAGE3	Between Groups	4.337E-02	3	1.446E-02	2.285	.156
	Within Groups	5.060E-02	8	6.325E-03		
	Total	9.397E-02	11			

Table 31 Multiple comparisons between oxidation indices – 3 months

STORAGE3

Duncan[a]

TREATMEN	N	Subset for alpha = .05	
		1	2
2	3	.1500	
3	3	.2233	.2233
1	3	.2667	.2667
4	3		.3133
Sig.		.123	.220

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 3.000

G.4.3. After 6 months storage

Table 32 ANOVA Table of oxidation indices – 6 months

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
STORAGE6	Between Groups	4.096E-02	3	1.365E-02	17.808	.001
	Within Groups	6.133E-03	8	7.667E-04		
	Total	4.709E-02	11			

Table 33 Multiple comparisons between oxidation indices – 6 months

STORAGE6

Duncan[a]

		Subset for alpha = .05	
TREATMEN	N	1	2
1	3	.2000	
2	3	.2033	
4	3	.2133	
3	3		.3400
Sig.		.587	1.000

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 3.000

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