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dissertation entitled

IDENTIFICATION OF OFF-FLAVOR COMPONENTS FOUND IN  
MILK PACKAGED IN GABLE-TOP  
PAPERBOARD CONTAINERS

presented by

Hasand Gandhi

has been accepted towards fulfillment  
of the requirements for

PhD degree in Food Science

  
Major professor

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IDENTIFICATION OF OFF-FLAVOR COMPONENTS  
FOUND IN MILK PACKAGED IN GABLE-TOP  
PAPERBOARD CONTAINERS

By

Hasand Gandhi

A DISSERTATION

Submitted to  
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## **ABSTRACT**

### **IDENTIFICATION OF OFF-FLAVOR COMPONENTS FOUND IN MILK PACKAGED IN GABLE-TOP PAPERBOARD CONTAINERS**

By

Hasand Gandhi

Two percent fat milk packaged in half-pint polyethylene coated, paperboard cartons were evaluated by school children using a two sided, paired preference test and a nine point Hedonic scale. Half-pint cartons obtained from the three major carton manufacturers were filled with water and evaluated by an 11-member trained sensory panel using a paired comparison test. Milk and water stored in glass containers were used as controls. All samples of milk and water were stored for 3 d at 2.2 °C before being subjected to analysis. The pooled data for 2nd through 5th grades showed that the elementary school children had a higher preference ( $p < 0.01$ ) and acceptability rating ( $p < 0.05$ ) for the control versus the milk stored in cartons. The packaging flavor was also detected by the trained panel ( $p < 0.05$ ). The extent to which packaging flavor developed varied with the manufacturer of carton.

The water samples were also analyzed using purge and trap technique for trapping of the volatile compounds. The trapped volatiles were then either desorbed directly onto the gas chromatograph or concentrated using solvent extraction before being analyzed by gas chromatography and mass spectrometry.

Hasand Gandhi

The chromatogram's obtained from the gas chromatographic analysis of the water samples exhibited the presence of peaks which were not present in the control samples. This was due to the migration of the volatile compounds from the package to the enclosed product during storage. The group of migrating compounds identified by mass spectrometry included, aliphatic hydrocarbons; aromatic hydrocarbons; phenol; and ester. The concentration of these compounds varied between different cartons from the same stock, and also between cartons obtained from different manufacturers. Concentration of compounds isolated from half-pint (236 ml) water samples was in parts per billion range.

**To my loving wife Cheryl and son Nicholas.**

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## INTRODUCTION

Food packaging has undergone a dramatic change in the last two decades. The expanding use of plastic materials for food packaging has made the products convenient to handle, but has also posed problems of off-flavors in the goods originating from the package. Most plastic materials used in food packaging are inert, but the polymerization causes the formation of low molecular weight constituents capable of migrating through the package and thus causing off-flavors in foods. The large number of additives used in the polymer industry may also be transferred to the food, forming off-flavors. Processing of the polymers at high temperature may lead to their partial degradation and to the appearance of oxidative products capable of further decomposition. Small amounts of solvents used during lamination, coating, or lacquer applications may still remain in the material. Excessive reuse of plastics may cause off-flavors in such films as polyethylene (PE) and polypropylene (PP) (Peled and Mannheim, 1977).

Good tasting milk that also meets all requirements set forth in the law is characterized as having a pleasant, slightly sweet taste with no unpleasant aftertaste.

However, its bland nature makes it very susceptible to flavor defects from a variety of sources (Bassette and Mantha, 1986). Consumer acceptance of a food is largely determined by flavor rather than nutritional content, primarily because flavor can be easily judged. Pasteurized milk, being bland in nature sets high requirements on flavor neutrality of the packaging materials. The limits of low molecular weight substances in plastic materials, which can migrate into packaged foods, is set from the point of view of health protection. However, the concentration of these substances, which may cause off-flavors in packaged foods with weak characteristic flavor are often substantially less than the maximum tolerable quantity from the health aspect (Bojkow et al., 1976).

The expansion of the institutional market, including schools, has caused a tremendous increase in the number of half-pints consumed. With the exception of gallons and half gallons, more fluid milk products are sold in half pints than any other size of container (U.S.D.A., 1994). In 1993, monthly 358 million pounds of fluid milk products were sold in half-pint containers. Of the total half pints sold, 97 percent were in polyethylene coated paperboard cartons and the rest 3 percent in plastic containers (U.S.D.A., 1994). Approximately 6.6 percent of fluid milk sales in 1993 were delivered to schools and 9.4 percent of milk was sold in half-pint containers (U.S.D.A., 1994).

It was reported that more than 5.5 billion half pints of milk were served to 43 million U.S. school children each year accounting for 10% of the total fluid milk sales during the school year. The national average was 0.7 half pint per pupil per day. Therefore, if each child drank 1.0 half pint per day, a potential sales gain of 2.2 billion half pints of milk per year could be realized. Better consumption was not achieved because many children said they disliked milk, especially at school. Some asked their parents not to buy the same milk as served in the school (Bandler et al., 1975).

Birch (1987) reported that patterns of food acceptance in humans are largely acquired and a great deal of the acquisition process occurs during the early years of life. Children must learn what to eat, when to eat, and how much to eat. This includes the acquisition of affective reactions to food-conditioned preferences and aversions. Eating habits are established during the early childhood years and are probably resistant to change in later life (Hodgson and Nelson, 1985). The presence of off-flavor in milk may discourage milk consumption in children, who are traditionally heavy milk drinkers. Someone who does not like milk as a child is not likely to be a milk drinker as an adult, when habits are difficult to change. The quality of milk should be maintained; and it should reach the consumer in the best possible organoleptic (appearance, odor, flavor) condition and should be wholesome.

This study was undertaken to test the hypothesis: "Milk packaged in polyethylene coated paperboard containers develops a packaging flavor due to migration of compounds from the packaging material into milk. This off-flavor is perceptible and discourages the milk consumption in children, who are traditionally heavy milk drinkers."

The objectives of this study were:

1. To survey consumer populations, especially school children, to find the extent of off-flavor perception resulting from the packaging of milk in polyethylene coated, paperboard containers.
2. To survey consumer populations, especially school children, to learn flavor preference for milk based on the type of package used.
3. To develop a technique to isolate the volatile compounds migrating from milk cartons to the enclosed product.
4. To identify the off-flavor components which contribute towards the packaging flavor detected in milk packaged in PE-coated paperboard containers.

## **LITERATURE REVIEW**

### **1. HISTORY**

The glass bottle, introduced in 1878, was the first package used for distributing milk to the consumer (Prucha and Tracy, 1943). The paper milk container was invented by G.W. Maxwell of San Francisco and first used by dairyman in Los Angeles (Winslow, 1909). Paper containers had several advantages, which included break resistance, light weight, easier handling, and disposability, which eliminated bottle collecting, washing and sanitizing. By the late 1930's, the paper container was generally accepted by both industry and milk sanitarians (Sanborn, 1942).

While about 30 different varieties of paper milk containers have been developed, only 5 were in everyday use in the late 1930's. Containers commonly used were generally of two shapes, rectangular or round. The former had either a flat or gable top. These were the Canco<sup>®</sup> and Pure-Pak<sup>®</sup> containers. There were three round types, two of which were nearly identical, cone shaped and were known as Sealright<sup>®</sup> and Pure-cone<sup>®</sup> containers. The other round container, the Reed<sup>®</sup>, was cylindrical with a folded star-shaped top, and sealed with a metal fastener (Sanborn, 1942). Paraffin wax



was soon replaced by vinyl and later by polyethylene (PE) as a coating for paperboard. Important properties of PE included chemical inertness, toughness, flexibility, water resistance, and heat sealability.

The first gable-top carton was developed by the Ex-Cell-O corporation in 1936. The square, plastic-coated paper cartons (Sealking containers) developed by Sealright Company, Inc. of Fulton, New York were available to the market nationwide in 1949 (Anonymous, 1949). The gable-top paperboard carton was found a convenient, high quality package. Strength, stability, product protection and graphics capabilities made it the package of choice for many liquid products.

## **2. OXYGEN PERMEABILITY OF MILK PACKAGES**

### **2.1 Type of packaging**

The type of packaging used for commercially pasteurized milk can affect the concentration and consumption of oxygen in milk. Apart from the traditional glass bottle, aluminum and/or polyethylene laminated paperboard packages and all-plastic containers are in use today in liquid milk packaging. The PE sachets and PE-coated cartons possess greater permeability to oxygen than aluminum lined cartons (Mehta and Bassette, 1978; Allen and Joseph, 1985). Storgards and Lembke (1966) investigated the protective influence of different packaging materials on the oxidation

processes of milk. Aluminum laminated paper was practically gas-proof, followed by milk-colored plastics and clear plastic cups and paper packages coated with polyethylene.

Fluckiger (1972) compared liter PE coated cartons with aluminum foil (AC) and without aluminum foil (PC) for storage of UHT milk. Aluminum foil laminated paperboard cartons did not lose any weight during six weeks of storage, while PC cartons lost 0.2% weight at 20°C and 1% at 38°C. Oxygen was unchanged (1 ppm) in AC cartons while in PC cartons, milk was saturated with oxygen (8-9 ppm) after a few days. Most of the oxidative changes in PC cartons took place in the first 2-3 days after processing. The reducing substances in the milk that offer protection against oxidation decreased rapidly in PC cartons. The UHT milk was organoleptically acceptable up to 3 weeks when stored at 15°C in PC cartons whereas milk in AC cartons was acceptable for 2 months, even at a storage temperature of 38°C.

The oxygen permeability of milk packages was investigated by Fluckiger and Heuscher (1966). They found only slight difference in the oxygen permeability among PE-coated papers (Tetra Pak®, Zupack®, and Pure-Pak®). The paraffin-coated material (Perga®) was found significantly more permeable. The oxygen content was lowest in milk packaged in Zupack® and highest in Perga® after twenty four hour storage. The oxygen content remained low (0.4 ppm) in aluminum-lined Tetra-Pak® cartons whereas, it increased rapidly to eight ppm in non aluminum-lined Tetra-Pak®

cartons.

The oxygen permeability of various milk containers filled with water was evaluated by Hansen (1975). He reported a 26, 11, and 35% loss of oxygen pressure inside the Pure-Pak®, Pure-Pak® with aluminum foil, and Tetra Brik® after 24 hour storage. Schroder et al. (1985) reported that milk packaged in quart Pure-Pak® cartons at filling was generally saturated with oxygen. However, if no additional oxygen could gain access, its content fell and the rate of the adverse reactions slowed or stopped. However, additional oxygen from a headspace or entering through a permeable container would maintain the oxygen content and keep the rate of oxidative reactions high.

## **2.2 Storage environment**

The quality of milk of the same origin in different packaging systems was investigated as a function of the storage conditions during periods extending over 8 days. The major difference in packaging was the air space in the package above the milk. System A had no air space; system B (upright pack) had a milk/air interface of about 49 cm<sup>2</sup> and system C (oblong pack) interfaced about 71 cm<sup>2</sup>. Sensory analysis showed that flavor of milk of system A was superior to others after 1 day storage at 4 to 5°C. There was a connection between milk quality and the level of filling in the package. Milk in packages without an air space usually had a quality superior to that in packages with an air space

(Schonborn et al., 1975).

Dejmek and Anas (1977) reported a small contact surface between milk and headspace oxygen in one liter Pure-Pak<sup>®</sup> cartons. Due to a slow diffusion of oxygen through milk, headspace oxygen exerted little influence on the oxygen content of milk. The carton walls and package conditions were the causes of oxygen transfer. The convection currents arising from small temperature difference between the inside and outside of the package wall increased oxygen transfer three-fold. The oxygen transfer increased five-fold when the carton was shaken.

### **3. OFF-FLAVOR DEVELOPMENT DUE TO LIGHT PENETRATION**

Milk Packaged in glass, polycarbonate, high density PE, blow-molded PE, plastic bags and paperboard containers, when exposed to fluorescent light or sunlight, will develop a characteristic off-flavor described as activated, sunlight or oxidized flavor. The extent of flavor development is related to the exposure interval, strength of the light and amount of milk surface exposed.

The milk stored in paper bottles and containers used during 1930's developed off-flavors like tallowy (Doan and Myers, 1936), sunshine (Tracy, 1938) and sunlight (Guthrie et al., 1939), due to exposure to light rays. The inner surface of paper bottles was treated with paraffin containing 25 % oat flour by Dahle and Palmer (1937). This

treatment prevented oxidized flavor in milk exposed to sunlight for one hour. Similar results were reported by Dahle and Josephson (1939); Garrett (1940) and England and Wiedemer (1941). Prucha and Tracy (1943) reported that milk stored in heavy-weight papers (basis weight) was less affected by sunlight as compared to milk stored in light weight papers. The use of dark red and brown cartons for milk packaging remarkably reduced the detrimental effect of light (Wildbrett, 1960; Koenen, 1967).

Fluorescent light exposure also can cause oxidized flavor in milk. The minimum time required to induce detectable light flavor was 1-14 hours for several unprinted fiberboard milk cartons coated with paraffin or PE (Dunkley et al., 1962). Best protection was provided by cartons with large areas printed with inks (yellow, red, orange, and brown) that absorb shorter wavelength light. Hendrick and Moor (1962) reported that milk stored in Tetra Paks® with black inner coating when exposed to fluorescent light provided almost complete protection against off-flavor development. Use of brown, yellow, and red colored containers provided slightly less protection.

Bradfield and Duthie (1965 and 1966) tested the PE-coated cartons in solid colors (plain, red, blue, black and green). Green cartons gave the lowest light transmission values thus providing the greatest protection. They also concluded that the container with the aluminum foil top gave better protection than the container with the plain top.

Half-gallon cartons were found to provide better protection for the milk than the quarts due to lower light transmission because of less surface area in relation to volume. Sattar and deMan (1973) reported off-flavor development in milk in quart containers after 12 hour exposure of 100 footcandles (ftc) of light.

Barnard (1972) reported an increase in the incidence of oxidized flavor in milk in plastic coated, paper containers. This increase was attributed to use of pastel colors on white on the gable of the containers. He recommended use of paper containers with a built in layer of aluminum foil to block out the light. Coleman et al. (1976) exposed pasteurized, homogenized milk packaged in unpigmented and variously colored paperboard and blow molded plastic containers to fluorescent light. They found significant differences ( $p < 0.05$ ) among various colored paperboard containers. The unpigmented, yellow, and red offered less protection to light-induced flavor changes than the other colors (black, blue, green, orange, purple and brown) investigated.

DeMan (1978) studied the effect of light on milk packaged in different types of packaging materials. Three commercially available packages, carton, plastic pouch and returnable plastic jug, were used as well as cartons with inner brown printing, plastic pouches with black pigmented overwrap and plastic jugs pigmented with titanium dioxide. The colored carton and pigmented pouch pack had a light

transmission over the whole visible spectrum of less than 1% and were very effective in preventing light induced changes in the milk. The pigmented jugs were not found satisfactory. A comparison was made of four major types of containers and the distribution of oxidized flavor in packaged milk by Bradley, (1980). Eighty six percent of milk packaged in blow-molded plastic containers was criticized as having an oxidized flavor. These percentages were 50%, 46.4% and 12.7% for milk packaged in plastic bags; glass bottles and plastic coated paper, respectively. It was also suggested that in paperboard containers, the ink used absorbs light energy. Cartons should be designed with large areas of red, brown, black, yellow or orange inks to absorb the shorter wavelengths of energy. This was found particularly true of the top or gable of the carton.

Nelson and Cathcart (1983) measured the light transmissions through milk carton paperboards, milk cartons, and blow molded PE containers. Yellow, orange, gold, red, brown and black inks were found to opacify the half gallon cartons to wavelengths below 500 nm. Light transmission was reduced throughout the visible region by black, brown, and blue inks. Light contacting milk reportedly caused chemical reactions leading to changes in flavor as well as loss of vitamins and other nutritional components. Therefore, the composition of the container used to hold milk was critical. Milk cartons with large printed areas were found to provide good light protection for the milk. Nelson and Cathcart

(1984) confirmed their earlier studies, and reported that pigmenting PE milk containers with titanium dioxide resulted in a substantial reduction in the light reduction. Commercially pasteurized, non-homogenized full cream milk in 2-pint white PE coated cartons overprinted with blue, and in 4-pint PE bottles was stored for 4 days in the dark or under white fluorescent light of 4000 lux, at a temperature of 7°C (Schroder et al., 1985). The flavor of milk kept in the dark remained good, but exposure to light resulted in early off-flavor development. Cartoned milk was disliked by a flavor panel after about 17.5 hours exposure and milk in the PE bottles after 9 hours.

#### **4. OFF-FLAVOR DEVELOPMENT DUE TO PACKAGING INTERACTION**

Expanding use of plastic materials for food packaging has posed problems of off-flavor in the goods stored in the package. This has created the need for research into potential interactions that might arise between food and packages and the effects that these might have on food quality. Loss of flavor components due to sorption by plastics may be important. Salame and Temple (1974) reported that a 1% loss of an aroma component to packaging results in a change in the quality that is detectable to the human olfactory senses. While the emphasis in aroma sorption has been of citrus aroma components by plastics, research describing the effect of the plastic-coated cartons on the flavor of milk and other dairy products is meager.



#### **4.1 Type of plastic films**

Wildbrett (1968) reported that during direct contact between plastics and food products, low molecular weight components may migrate from plastics. These compounds can adversely affect the organoleptic properties of the food products. Figge and Baustian (1983) tested the films made of low and high density PE (LDPE and HDPE); polypropylene (PP); high impact polystyrene (HIPS); and polyacetal (POM) with addition of various phenolic additives. These films were kept in contact with raw milk, fresh unskimmed milk, sterilized milk and cocoa drink, and water under storage conditions of 7 or 21 days at 20°C. The amount of additives that migrated under the storage conditions from plastic materials were measured radioanalytically. It was reported that under the practical conditions roughly comparable amounts of additives migrated from each tested plastic materials into the various foodstuffs and water. The amounts of additives that migrated from the plastic materials into water corresponded very well with the amounts that were found in different kinds of milk and cocoa drink after storage under practical conditions.

Durst and Laperle (1990) reported a plastic like off-flavor in apple juice packaged in multilayered polystyrene containers. This off-flavor was predominantly caused by residual styrene monomer, together with ethylbenzene, that had diffused into the food product.

Kwapong and Hotchkiss (1987) investigated sorption of

aroma by three common food packaging plastics in an aqueous system. All plastics (LDPE and 2 ionomers), were found to have similar sorption behavior. They concluded that the sorption of aroma compounds by the three food contact plastics changed the character and intensity of the complex aroma. For the three plastics studied, the nature of aroma compounds was more important in deciding the extent of sorption than that of the plastics tested. However, this does not necessarily hold for all polymers especially those that are below their glass transition temperatures. For such polymers, adsorption will most likely be the controlling mechanism.

Marin et al. (1992) reported that single strength, not from concentrate orange juice packed in glass containers offered better product quality than frozen concentrated juice but at higher container and shipping costs. This was due to absorption of flavor by the polymeric packaging materials. Loss of orange juice flavor was related to the absorption of d-limonene, a major orange juice volatile, into the polyolefin packaging.

#### **4.2 Polyethylene**

Milk packaged in polyethylene containers developed off-flavor which was described as, plastic (Kiermer and Stroh, 1969; Srivastava and Rawat, 1978), off-flavor (Hansen et al., 1974; Peled and Mannheim, 1977; Berg, 1980), bitter (Chuchlowa and Sikora, 1976), and oxidative (Bojkow et al.,

1976; Bojkow et al., 1977).

Kiermer and Stroh (1969) tested the suitability of the PE for packaging of milk. The PE tested had a density of 0.918-0.931 and a melt index of 0.2 - 20. They were able to prove the presence of different compounds especially ketocarbonyl and carboxyl groups, which were found to exchange their weak acidic protons with metallic cations. In milk too, an ion exchange between the metallic cations of milk salts and the acidic protons of the carboxyl groups in oxidized polyethylene could be detected. Ion exchange was found to increase with an increase in melt index and a decrease in density of the PE. Resulting from this autoxidation of PE, non-branched carboxylic acids with carbon numbers C14, C19-C21, C24-C26 and C38-C42 were detected as decomposed products in water solutions, which were thought to be responsible for the plastic flavor sometimes found in milk packaged in PE. PE was found to be suitable for packaging milk when the density, melt index, and technical management of the product were properly coordinated.

Hansen et al. (1974) reported that PE bags did not give satisfactory results for prolonged storage of fluid milk. Some flavor absorption problems were encountered when PE bags were used. However, flavor absorption in PE jugs occurred at a much lower rate. UHT milk packaged in a PE bag and cardboard box showed noticeable flavor absorption after 16 days. Most of the cooked flavor had dissipated,

and the milk was bland at this time. There was no masking effect of the heated taste, and off-flavor became very noticeable. Flavor became more intense as the storage period increased. It was suggested that possibly the sizing glues and components in the cardboard were absorbed through the PE film. The flavor problem was eliminated when sterile amber and clear glass containers were used.

Chuchlowa and Sikora (1976) noticed a slight bitter off-flavor in milk packaged in PE pouches after three days of storage. Peled and Mannheim (1977) reported that standard (2.7%F) and skim milk packaged in commercial PE bags and stored in a refrigerator developed off-flavor after 2 days of storage, but no off-odor was detected. Bags stored in the same refrigerator in a closed vessel did not develop any off-flavor during 6 days of storage. This off-flavor might have developed due to the permeability of the film to flavors from the refrigerator. They were not able to find any extractable material in distilled water, but water had considerable off taste. This was probably due to the low concentration of the constituents causing off flavors. Thereby, the injection of the water extract into gas liquid chromatograph gave no results. Srivastava and Rawat (1978) studied the organoleptic quality of milk and physical characteristics of plastic pouches for in-package processing of milk and reported that the PE in the paper/aluminum/PE laminates imparted pronounced plastic flavor to milk.

### 4.3 Polyethylene coated paperboard cartons

Bojkow et al. (1976) conducted organoleptic examinations of PE-films for milk pouches and PE-coated papers and boards for milk packages. A high frequency of lots were found affecting the taste of pasteurized milk. The character of the off-flavor was the type caused by oxidative changes of the PE surface. Platinol AH, which was found as an additive in coloring matters or printing colors in the inner layer of PE-films and PE-coated papers, seemed to have a masking effect on the identification of flavor transfer caused by oxidative changes of the PE-surface.

Fresh pasteurized milk contained in paperboard packages and PE coated cartons in various circumstances presented a taste, particularly moldy, bitter and astringent, which had never been remarked when it was exclusively placed in bottles. They conducted an organoleptic examination of 65 PE films and coated papers. 46% of the samples were found to adversely effect the flavor of milk with which they had been in contact (Bojkow et al., 1977).

Berg (1980) reported that products like milk, water and fruit juices, frequently revealed an unfavorable reaction of off-taste when stored in bottles of PE or PE-coated cartons. He tried to determine if off-flavor was intrinsic to plastics raw material or was due to the conversion process or the use of additives. He found that the off-flavor

compounds were already present in the PE granulate and most probably did not come from solvents or additives used in the polymerization step during the manufacture of packaging material. Also the converting/extrusion process made only a small increase in the amount of off-flavor volatiles.

Leong et al. (1992) used a ten member trained panel to evaluate the milk packaged in PE-coated paperboard containers. Milk (2% fat) in both half-pint Echo-Pak<sup>R</sup> and standard cross-section cartons had more "cardboardy" off-flavor than in glass containers ( $p < 0.01$ ). Similar results were obtained for skim-milk, whole milk and water. The off-flavor was more pronounced in water and skim-milk. Milk (2% fat) packaged in half-pint cartons was more "cardboardy" than the milk in quart and half-gallon cartons after 3 days of storage at 36 °F ( $p < 0.01$ ). No further significant increase in the off-flavor of milk in half-pint cartons was observed after 3 days. The half pint cartons had a surface area:volume ratio of 0.84 cm<sup>2</sup>/ml, which was much higher than the quart (0.59 cm<sup>2</sup>/ml) and half-gallon (0.45 cm<sup>2</sup>/ml) cartons. They reported that flavor problems due to migration from package components would increase with decreasing container size. This resulted because of an increase in surface area:volume ratio of the container. This off-flavor was not due to storage temperature, lipid oxidation or excessively high heat-sealing temperatures.

Mehta and Bassette (1978) investigated the effects of Carton materials on flavor of UHT sterilized milks stored

for 100 days at  $22 \pm 2^{\circ}\text{C}$ . Flavor scores of stored milk decreased concurrently with an increase in stale flavor. The concentrations of propanal, pentanal, hexanal, and an unidentified compound increased; whereas cooked flavor along with methyl sulfide and another unidentified compound decreased. The abnormally high acetaldehyde concentrations were related to the ethylene oxide sterilizing pretreatment of the carton board. Aluminum foil-lined cartons were found less permeable to gases than were PE lined cartons. Milk packaged in aluminum foil lined cartons retained desirable flavor characteristics longer than did that stored in PE lined cartons. Generally, as the stale flavor increased, the cooked flavor decreased for the UHT milks. They suggested that aluminum foil lining was slightly permeable to gases, probably through microscopic pores in the aluminum foil lining. However, plain PE-lined cartons were more permeable to gases than the aluminum foil lined cartons. UHT milks exhibited two types of off flavors; (a) cooked from volatile sulphydryl compounds induced by heat, such as methyl sulfide; and (b) stale caused by volatile carbonyl compounds produced from the milk, from one or more of the carton layers. Mehta and Bassette (1980) later confirmed their prior studies. They also reported that increase in off-flavor intensity paralleled the increase in concentration of n-pentanal and an unidentified neutral volatile compound.

Mannheim et al. (1987) evaluated the quality of citrus

juices (orange and grapefruit) aseptically packed into laminated cartons and glass jars and stored at three temperatures. The extent of browning and loss of ascorbic acid was greater in cartons than in glass. The d-limonene content of the juices in cartons was reduced by 25% within 14 days of storage due to absorption by PE. Sensory evaluation showed a significant difference after 10-12 weeks between juices packed in glass and cartons stored at ambient temperatures. The shelf life of juices in carton packs was shorter (about half) than in glass packages, and was usually not more than 3-4 months at ambient temperature. The low shelf life of juices stored in laminated cartons was due to absorption of d-limonene by the PE contacting surface; acceleration of ascorbic acid degradation and browning due to contact with PE film; and the transmission of oxygen through the package.

#### **4.4 Paperboard**

Janzen et al. (1981) conducted shelf-life studies on commercially pasteurized milk packaged in fiberboard and blow-mold plastic containers. The samples were stored at 4.5 and 7°C for 0, 7 and 14 days. No significant ( $P > .01$ ) differences, in the flavor score, were noted between milk packaged in fiberboard and plastic jugs that were not exposed to fluorescent light. The statistical analysis of the data revealed that in the first phase of the study there was no significant ( $P > .10$ ) effect of container type on any



of the measured quality parameters. However, a closer look at the data for flavor score and acid degree value (ADV) revealed that mean flavor scores for the milk in both containers were about the same. The plastic jugs exhibited a slight edge over the cartons after 7 and 14 days of storage. The mean flavor scores for milk stored in plastic jugs without exposure to fluorescent light were equal to or slightly higher than for the milk packaged in fiberboard containers.

Simon and Hansen (1995) studied the effect of six different packaging boards on the shelf life and flavor of pasteurized milk obtained from three different manufacturers. They performed standard plate counts (SPC) and taste panels on the milk samples weekly for one month. It was concluded that all off flavors detected in milk samples were due to the microbial spoilage and the use of different type of packaging boards did not affect the off-flavor development.

Giacin and Gilbert (1973) identified PCBs (polychlorinated biphenyls) in samples of packaged food. The origins of these contaminants were traced to the presence of these compounds in paperboard made from recycled paper. One source of PCB was the inclusion of "carbonless" carbon paper (which used PCBs in its formulation) in the recycling process. Another source of PCBs was from the printing inks.

Vaccaro (1980) identified several volatiles released

from PET-coated paperboard during heating. When the paperboard and PET films were analyzed separately to establish the origin of the released volatiles, no volatiles were detected from the PET film used for the coating. All of the volatiles detected were released from the paperboard. Eight compounds were identified: acetone, 2,3,-butandione, chloroform, furan, furfural, methylene chloride, carbon disulfide, and acetaldehyde. It was suggested that the chlorinated compounds may be present because of the board bleaching process, and the carbon disulfide because of the sulfate pulp process to remove lignin.

Whitfield et al. (1984) observed a disagreeable odor in cocoa powder and traced the source to the presence of chlorophenols and chloroanisoles, contaminants derived from the paper and adhesives used in the construction of the sacks. The principal cause of the "moldy" off-flavor was 2,4,6-trichloroanisole present in the tainted cocoa powder. The chlorophenols such as 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 2,3,4,6-tetrachlorophenol are considered formed during the bleaching of wood pulp for paper manufacture (Voss et al., 1980), and pentachlorophenol is a biocide frequently used in adhesives (Freiter, 1979).

Entz and Diachenko (1988) while attempting to find residues of volatile halocarbons in margarine, found one of the major sources to be the exterior paperboard packaging to which adhesive was applied. The outer packaging contained up to 2500 times as much methylchloroform compared with the

inner wrapper, usually a foil laminate.

## **5. METHODS FOR ISOLATION AND IDENTIFICATION OF VOLATILES**

The analysis of flavor in packaging materials generally involves headspace gas chromatographic techniques (Kang, 1990). This technique has been found simple and reproducible. However, due to the limited amount of headspace gas that can be injected into the gas chromatograph (GC), low sensitivity is achieved using this method (Hartman *et al.*, 1993). The detection threshold capabilities of GC detectors and mass spectrometers (MS) prevent the 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. Due to these reason's enrichment techniques collectively called dynamic headspace analysis have been developed. These techniques involve a means of concentrating headspace aroma volatiles prior to GC analysis.

The methods used for the isolation of flavor concentrates have been categorized under three general headings (Sugisawa, 1981). The three categories are: (1) distillation techniques, including vacuum distillation; steam distillation and carbon dioxide distillation; (2)

extraction techniques, including solvent extraction, simultaneous steam-distillation-solvent extraction, carbon dioxide, and supercritical fluid extraction; and (3) miscellaneous techniques, including gas entrainment in open and closed systems, and adsorption on charcoal and porous polymers.

A technique for enriching headspace flavor volatiles that has grown in popularity is the use of porous polymer adsorbent trapping and direct thermal desorption. Van Wijk (1970) introduced a thermally stable porous polymer named Tenax-GC (poly[2,6-diphenyl-p-phenylene oxide]) for use as a GC stationary phase. Tenax-GC had a high adsorptive capacity toward volatile and semivolatile organic compounds and a low affinity for water vapor. Due to these properties, Tenax has been used as a trapping medium for isolating and concentrating volatile organics in food, environmental, and biological samples (Hartman *et al.*, 1993). Besides Tenax, other adsorbents like activated carbon, silica gel, and other porous polymers have been used as trapping media, alone or in combination. The purge and trap-thermal desorption (P&T-TD) technique involves the sparging of the solid and liquid samples 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 into a gas chromatograph for analysis providing greatly increased sensitivity relative to static

headspace measurements.

Hartman et al. (1991) described a short path thermal desorption system developed by Scientific Instrument Services Corporation, in cooperation with Rutgers University's Center for Advanced Food Technology. This system could be attached to the injection port of a GC, and used for qualitative and quantitative determination of volatile and semivolatile components in foods, packaging materials, and other matrices.

Bertoni et al. (1981) evaluated the mutual influence of organic compounds present in the atmosphere on their breakthrough volumes when trapped on light adsorbents. They found that the light adsorbents such as Tenax GC (Enka, Arnhem, The Netherlands) and Carboxpack B (Supelco, Bellefonte, PA, USA) were particularly useful at room temperature for the evaluation of air pollution. The desorption oven temperature however, had to be kept constant within 10°C. The desorbing temperature was determined by the molecule size and vapor pressure of the compounds to be monitored. They suggested that the traps should be stripped with the carrier gas flowing in the opposite direction to that used in sampling, i.e., they should be back flushed. Finally, flash heating at a higher temperature was preferred to slow heating at lower temperatures. Some studies using these techniques have been summarized below.

Vercelloti et al. (1987) used purge and trap (P&T)-TD 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 in a Tenax containing glass lined trap. The trap was later heated and volatiles purged into a GC-MS system for identification and estimation of concentration. They were able to identify more than 50 heteroatomic, mostly cyclic compounds. Kuo *et al.* (1989) developed a simple and selective P&T method for isolation, concentration, and fractionation of volatile pyrazines generated from a model system and potato chips. The volatiles trapped in the adsorbent trap were then subjected to thermal desorption for GC and GC-MS analysis.

Booker and Friese (1989) reported a simple P&T-TD procedure for analyzing the volatile compounds generated by heating microwave susceptor packages. After microwave irradiation or conventional heating, the vial containing the sample was placed unopened into an oven at 40°C for 16 hours. The volatile compounds were quantitatively collected on Tenax; desorbed into the injector of a GC and subsequently identified by their MS and retention times. They suggested that trapping the volatiles in a closed reaction vessel and then desorbing them in a GC inlet was a sensitive and simple procedure upon which to base a satisfactory protocol. Analyzing the volatiles by transferring an aliquot of the headspace gases reduced the time of analysis, but at an expense of sensitivity. Durst

and Laperle (1990) used P&T-TD system to measure the concentration of styrene monomer that migrated from the multilayered polystyrene containers into the apple juice, over time.

Krzymien and Elias (1990) developed a simple but precise procedure for measuring the headspace concentration of trimethylamine (TMA) concentration in fish tissue. The method was based on air sampling with Carbotrap or Tenax sorbent tubes and subsequent thermal desorption and GC analysis. The sampling and analysis time was less than 5 minutes. Fish freshness found by this technique was consistent with grading estimated by sensory tests.

Connick and French (1991) identified the fragrance volatiles responsible for the sweet aroma produced when Canada thistle plants were infected with the systematic sexual stage of the Canada thistle rust, a prospective biological control agent for that weed. The identification was done using a capillary GCMS after thermal desorption from Tenax. Tenax trap tubes consisted of Pyrex glass tubes each packed with 0.10 g of Tenax GC porous polymer adsorbent held in place near the center with glass wool plugs. Tubes were reversed for subsequent thermal desorption so that volatiles were backflushed from the tube into the GC. Volatiles were desorbed from a Tenax trap tube at 200°C (3 min., 10 ml/min. He) in the external inlet unit and collected on the head of the capillary column, which was held at -30°C by dry ice in a wire basket placed in a column

oven.

Laye and Morr (1993) analyzed the volatile flavor compounds in the headspace of whey protein concentrate using a dynamic headspace analyzer, GC, and MS. They detected 32 compounds and the major flavor volatile compounds detected were 2-propanone, hexanal, and dimethyl disulfide. They tested different traps for their ability to recover volatiles. Both Tenax TA and Vocarb 3000 were found to recover volatiles in high concentration.

Brunner et al. (1978) compared the thermal desorption and solvent extraction techniques. They reported that thermal desorption method offers various advantages like: higher sampling flexibility; higher overall sensitivity; more homogeneous behavior to different substances; and higher overall sensitivity. Nitz et al. (1987) observed that the GC analysis of the volatile components of natural products (fruits, herbs, spices, etc.) required sample preparation procedures suited for GC such as solvent extraction, steam distillation, etc. These procedures were difficult and tedious to carry out on small amounts of sample. Contamination of sample with solvent impurities during extraction was often unavoidable. They suggested that the above shortcomings could be eliminated by using headspace analysis. The extraction of volatile components was achieved by stripping the headspace vial (8 ml capacity) with a constant helium flow (30 ml/min.), followed by cryogenic concentration in cooled ( $-130^{\circ}\text{C}$ ) trap, packed with



5% OV-101 on chromosorb W. The gas flow in the trap was reversed and enriched volatiles were introduced into the column by thermal desorption. After final separation, the substances were directed to the MS and/or sniffing mask. The advantages of this method were demonstrated using the suitable applications. The use of this technique allowed for fast analysis with minute sample amounts. No clean up procedure was necessary and contaminations with solvent impurities were avoided.

Nitz et al. (1991) described a system for thermal desorption with direct splitless sampling of sorption traps, containing airborne chemicals into a fused silica capillary column. The system when applied to flavor analysis (fresh yellow passion fruit), proved to be useful for detection of sensorially active trace compounds. A 500-1000 fold increase in the signal-to-noise ratio could be obtained with thermal desorption and splitless transfer on the capillary column as compared with solvent elution of sorption traps containing enriched substances and subsequent splitless liquid sample injection.

Nitz and Drawert (1986) described a variable effluent splitter for simultaneous sniffing-MS or GCMS. Simultaneous sniffing-MS monitoring was found to be a valuable approach, since the odor description and structural information could be obtained in a single run. The performance of the system was documented by application to trace analysis of relevant passion fruit flavor compounds.

Cormier et al. (1991) used P&T-TD, sniffing port and a GC equipped with a flame ionization detector (FID) to analyze the pleasant strawberry like odor produced by the organism (*Pseudomonas fragi*) when grown in skim milk at 15°C. They were able to isolate 90 different compounds, out of which 26 were found odor-active.

## **6. MECHANISM OF TRANSFER OF VOLATILES**

The flavor balance of a packaged food can be altered in three ways, viz; subtraction, reaction and addition. Subtraction occurs when components contributing to the desired flavor of the product are absorbed by the package (Moshonas and Shaw, 1989; Hriciga and Stadelman, 1988; Mannheim et al., 1988; Mannheim et al., 1987; Kwapong and Hotchkiss, 1987). Reaction takes place when package components chemically interact with food product to produce flavor artifacts. Sometimes the components in the packaging material, such as metal components, can act as a catalyst to accelerate the decomposition of food ingredients, resulting in undesirable flavor (Wiley et al., 1984). Addition occurs when the package releases compounds that alter the flavor balance of the food (Kim and Gilbert, 1989; Mcgorrin et al., 1987; Heydanek, 1977). Addition is by far the most common way of flavor disruption (Kang, 1990).

Clear polymers, used in the manufacture of composite packaging for milk, are by themselves insoluble but they contain small molecular substances that do not entirely

possess this property. The substances that under certain conditions may migrate from PE into milk and dairy products are: residues from the raw materials (monomers and their impurities, co-monomers); adjuvants in manufacture (initiators, stabilizers and antioxidants); adjuvants in transformation (lubricants, antistatics); colorants and pigments; and decomposition products (Bojkow et al., 1977; Kang, 1990).

## 7. Migration Theory

Fundamental processes by which trace amounts of solvents, reaction byproducts, additives, and monomers migrate from polymer barriers used in food and beverage packaging applications into the contents of a package have been discussed by several scientists (Downes, 1987; Gilbert et al., 1980; Koros and Hopfenberg, 1979). The classic theory of diffusion of gases is based on Fick's laws (Stannet, 1968). Diffusion in homogeneous substances is based upon the assumption that the rate of transfer,  $R$ , of a gas passing perpendicularly through the unit area of a section is proportional to the concentration gradient through the section. This is expressed as:

$$R = - D(C) \, dC/dX$$

where  $D(C)$  is the diffusion coefficient in  $\text{cm}^2/\text{s}$ , in general,  $D$  can be a function of the local diffusant concentration,  $C$  is the concentration of diffusant in  $\text{mol./cm}^3$ , and  $X$  is the thickness of the material in

centimeters.

The amount of package components that might migrate from a plastic packaging material into solid or liquid food or food simulating solvents would depend on the physical and chemical properties of both the food and polymer (Halek, 1988; Shepherd, 1982). The controlling factors for the degree of migration would be the original concentration of the migrants, the solubility in the contacting phase, the partition coefficient between the polymer and the contacting phase, the temperature, the time, and the morphological structure of the polymer (Chang et al., 1988; Gilbert et al., 1980).

Based on the limiting control mechanism, migration has been divided into three classes (Downes, 1987; Shepherd, 1982).

Class 1 -- Nonmigrating materials, with or without the presence of food

Class 2 -- Independently migrating not controlled by the food, although the presence of food may accelerate the migration

Class 3 -- Leaching; migration controlled by the food; negligible in the absence of food, significant in its presence

## **8. FAT CONTENT AND PERCEPTION OF PLASTIC FLAVOR**

Badings (1971) reported that the plastic flavor in milk packaged in polyethylene sachets, was observed more clearly

in proportion as the fat content of the milk was lowered. He recommended that the PE foil that was intended to be used as packaging material for milk was checked regularly for emission of flavor substances. Bojkow et al. (1976, 1977) conducted the organoleptic examinations of PE-films for milk pouches and PE-coated papers and boards for milk packages. The results showed a high frequency of lots affecting the taste of pasteurized milk. The intensity of this off-flavor increased with the decreasing fat content of the milk. But most of all it was found to effect the taste of pure water.

Milk packaged in PE-coated paperboard containers was evaluated by a 10-member trained panel (Leong et al., 1992). Milk (2% fat) packaged in PE-coated carton had more "cardboardy" off-flavor than milk packaged in glass containers. The perception of this off-flavor was reported to increase with the decrease in the fat content. The off-flavor was found to be more pronounced in skim milk and water.

#### **9. IMPORTANCE OF AIRING PACKAGING MATERIAL BEFORE FILLING**

Bojkow et al. (1976) conducted organoleptic examinations of PE-films for milk pouches and PE-coated papers and boards for milk packages. They observed a decrease of flavor transfer to the enclosed product when the packaging materials were stored for a longer period prior to filling. Bojkow et al. (1977) conducted organoleptic examinations of 65 PE films and coated papers. They

observed that the manufacturing processes, in particular the extrusion of coatings, increased the tendency of materials to transfer off-flavor. This effect was found to diminish with increased time between manufacture and use of the packaging material. Berg (1980) reported that products like milk, water, fruit juices, frequently revealed an unfavorable reaction of off-taste when stored in bottles of PE or PE-coated cartons. He found that the amount of these off-flavor volatiles decreased by up to 90% when the packaging materials were aired for 24 hours.

#### 10. TYPE OF FLAVOR COMPOUNDS

Bojkow et al. (1977) investigated the compounds responsible for the off-flavor in fresh pasteurized milk contained in paper packages and PE coated cartons. They detected the presence of Platinol AH (di[-2-ethyl-hexyl]phthalate) and Ionol (2,5-tertiary dibutyl-4-methylphenol) in almost all the materials tested. Platinol AH might accompany the pigments or printing ink used on the packages, whereas Ionol is used as an antioxidant. Bojkow et al. (1979) reported that the flavor components migrating from the internal PE coating were largely soluble in water and, they were volatile. However, the concentration of these compounds varied widely even in successive sections of continuously processed sheeting of packaging material or in successive blanks within a shipping-box. Due to this handicap the researchers were not able to establish

correlations between sensory and analytical results. The packaging materials from three major manufacturers were analyzed during this study. They separated about 120 components, in parts per billion (ppb) range. The off-flavor that was found typical for PE was not caused by one or a few components but by many different substances. The following organoleptically suspect classes of substances were isolated: unsaturated aliphatics, free fatty acids and compounds with alcoholic structures. These compounds occurred more frequently in materials strongly impairing the taste.

Berg (1980) reported that products like milk, water, fruit juices, frequently revealed an unfavorable reaction of off-taste when stored in bottles of PE or PE-coated cartons. The compounds identified in samples of PE-materials were divided into four groups: saturated aliphatic hydrocarbons (C-5 to C-13 both cyclic and noncyclic); unsaturated aliphatic hydrocarbons (C-5 to C-13 both cyclic and noncyclic); aromatic hydrocarbons (benzene, toluene, xylene, ethylbenzene, alkyl(C-3, C-4, C-5)benzenes); and aromatic hydrocarbons with an unsaturated side chain (alkyl(C-3, C-4, C-5) benzenes). He also identified volatile ketones and esters, which might have come from the inks used to print the cartons. Mehta and Bassette (1980) reported that an increase in off-flavor intensity of UHT sterilized milk packaged in PE-lined cartons stored for 1.5 months at 4°C, paralleled the increase in concentration of n-pentanal and

an unidentified neutral volatile compound.

Kim et al. (1987) identified a total of 33 compounds in the volatiles isolated from PVC. The groups of compounds identified included, aliphatic hydrocarbons; aromatic hydrocarbons; alcohols; ketones; aldehydes; esters; acids; and heterocyclic compounds. The most predominant volatile compounds were the breakdown products of two additives viz; bis-(2-ethylhexyl) adipate and tris-nonylphenyl phosphite. It was suggested that to produce PVC films of better odor quality, the type and amount of plasticizer and the processing temperature should be carefully controlled.

Booker and Friese (1989) studied the compounds released when microwave susceptor packages are heated. They reported that two classes of volatiles were released when the material was heated: thermally desorbed compounds that were indigenous to the material (residual chemicals from the papermaking process, solvents from adhesives, and contaminants arising from other sources) and products produced from the pyrolysis of paperboard coatings, inks, varnishes, etc.

## **11. SENSORY EVALUATION OF MILK**

Sensory evaluation is a useful technique that can help establish the worth of a commodity or even its acceptability. The principal uses of sensory methods are in quality control, product development, and research. This



technique has thus been widely used for characterization and evaluation of foods and beverages. Peled and Mannheim (1977) used sensory and analytical methods to study the off-flavors in milk samples, and concluded that the organoleptic tests were the most reliable tests for determination of the off-flavors originating from the packages. Sensory evaluation is an important tool used to identify causes of flavor defects.

#### **11.1 Time and temperature of storage**

Milk samples before being sensorially evaluated, were stored at 40°F, and examined at 24 hour intervals by Dahle and Palmer (1937). Sensory testing was continued until the off-flavor occurred or until the samples were discarded. Dunkley et al. (1962) stored the milk samples at 42°F for 24 to 48 hours, before presenting them to judges. Milk samples were stored at 7°C for 0 to 72 hours (Dimick, 1973; Hoskin and Dimick, 1978) or 4 days (Schroder et al., 1985) before being evaluated for the off-flavor development by the sensory panel. Milk samples were stored at 36°F for 3 days before being sensorially analyzed by the taste panel (Leong et al. 1992). Storage temperature of 5.6°C was used to evaluate the off-flavor development in milk samples, after storage of upto 4 weeks (Simon and Hansen, 1995).

## 11.2 Sample presentation and environment

Homogenized milk packaged in three half-gallon containers (Dimick, 1973) and five one-gallon containers (Hoskin and Dimick, 1979) was evaluated for development of light induced flavor under controlled exposure to fluorescent light for 3 to 72 hours. At each exposure time the containers were removed from the display case, mixed by inversion, and the aliquot transferred to 30-ml medicine cups in dim light. All samples were transferred and presented to the 12 panel members within 15 minutes. Tasting sessions were conducted in individual, partitioned booths maintained at 70°F and illuminated with red light to mask any color differences (Dimick, 1973; Hoskin and Dimick, 1979). Schroder *et al.* (1985) compared the protection against light-induced loss of quality afforded to pasteurized milk by the 2-pt PE-coated carton and the 4-pt PE bottle used in UK. Milk samples were presented to 8 judges in randomized and balanced order in coded containers at intervals over a 4 day storage period. Samples were warmed to 20°C, to allow proper appraisal of flavor, before being presented to the panel under red/blue light.

Peled and Mannheim (1977) compared milk stored in rigid polyethylene bottles, polyethylene bags and polystyrene cups to milk stored in glass bottles. They conducted the sensory evaluation studies in a well ventilated room with dim illumination. Leong *et al.* (1992) tested for the presence or absence of off-flavor in milk packaged in PE-coated

paperboard containers. Milk samples presented in randomized and balanced order in coded containers, were tasted by 10 judges in individual, partitioned booths under fluorescent light in a quiet, sensory evaluation laboratory maintained at 22°C.

Henderson et al. (1939) evaluated the influence of sunlight on flavor of milk exposed in three different type of paper containers. Milk samples were placed in half-pint glass bottles, keyed as unknowns, and placed in random order before being offered to judges for scoring.

### **11.3 Sensory Evaluation Techniques**

The American Dairy Science Association (ADSA) score card has been used for judging of milk samples by various researchers. Henderson et al. (1939) used the ADSA score card to identify and evaluate the effect of sunlight on flavor of milk exposed in three different types of paper containers. Feldstein and Johnson (1977) investigated the flavor problems during long term non-refrigerated storage of milk in various paperboard cartons. The taste panel graded the milk samples using an ADSA score card. Janzen et al. (1981) studied the interactions between time and temperature of storage on the shelf-life of milk. The judges scored the milk samples using an ADSA score card, using the 40 point flavor score.

Bandler et al. (1975) used the American Dairy Science scoring system as modified by the Tristate Milk Flavor

Program to evaluate the flavor of the milk served in New York public school system. The methods recommended by the American Dairy Science Association as modified for the Connecticut Milk Flavor Improvement Program were used by Hankin et al. (1980), for judging of flavor of milk served in Connecticut schools and camps. Mehta and Bassette (1978, 1980) used a modification of the National Collegiate Student Judging Contest procedure to study the effects of carton materials on flavor of ultra-high-temperature sterilized milk stored for 100 days at 22 °C.

The triangle test method in which the judge is asked to identify the odd-sample out of three samples presented to him, has been used by several researchers to conduct sensory evaluation studies. Fluckiger (1972) made a comparison of flavor of Uperized milk stored in cartons with or without aluminum foil. The tasters were asked to identify the two identical samples and the better tasting sample of the three samples presented. The triangle test was used to test water stored in glass containers against water stored in PE, for the possible off-flavor development due to contact with the packaging material (Berg, 1980). Mannheim et al. (1987) used triangle test with a 12-18 member taste panel to learn the difference in flavor between juices packed in glass jars versus cartons. The triangle test has been widely used for training and screening of judges for forming trained panels.

Sattar and deMan (1973) performed sensory analysis with a 12 to 18 member trained panel using the duo-trio test

difference analysis. The test was used to study the effect of four packaging materials - clear pouch, opaque pouch, carton and plastic jug, on milk quality deterioration on exposure to light.

England and Wiedemer (1941) scored milk samples for degree of sunlight induced oxidation, in order to determine the amount of oat flour treatment needed on paper bottles to prevent such deterioration. The degree of oxidation was expressed numerically on a four point scale (0=no oxidized flavor; 0.5=oxidized flavor may or may not be present; 1=definitely oxidized; 4=strongly oxidized). Wadsworth and Bassette (1984) investigated the role of dissolved oxygen as a contributor to flavor deterioration in sterile milk during storage. Milk samples were subjected to an organoleptic evaluation by a 4 member experienced taste panel. Each panelist was asked to evaluate the sample for any cooked, stale, and/or oxidized flavor on a scale of 1(none) to 4(pronounced).

Eight member trained panel evaluated milk samples exposed to fluorescent light for development of off-flavor based on a 4-point scale (0=none; 1=questionable; 2=slight; 3=distinct, objectionable; and 4=strong, very objectionable) (Dunkley et al., 1962). Hansen et al. (1973) used a 4 point scale (4=excellent; 3=good; 2=acceptable; 1=unacceptable; 0=very unacceptable) to evaluate the effect of ultra-high temperature steam injection on flavor acceptability of whole and fortified skim milks.

Bojcow et al. (1976) tested milk samples for flavor deterioration due to interaction with PE-films and PE-coated papers used for packaging. The intensity of flavor deterioration was estimated using a four point scale (0=no appreciable flavor deterioration at all; 1=scarcely appreciable flavor deterioration; 2=weak flavor deterioration; 3=notable flavor deterioration; and 4=strong flavor deterioration).

Bockelmann (1972) tested milk samples for overall quality by analyzing for four properties - appearance, consistency, smell and taste. These properties were ranked on a five-point scale (5=completely in accordance with product specification; 4=good agreement; 3=agreement; 2=minor deviations; and 1=major deviations) by the 3 judges. Garey et al. (1990) used a five point scale (1=terrible; 5=great) to rate the acceptability of the milk samples by the elementary school children in New York. They reported the acceptability rating to be a reliable method in predicting food consumption.

DeMan (1978) evaluated milk samples stored in combinations of packages and with different time exposures. They used a 9 point scoring system to rate the samples in relation to unexposed controls. A randomized block design with 12 to 18 panelists as blocks was constructed, and the data was subjected to analysis of variance.

Mehta and Bassette (1978, 1980) studied the effects of carton materials on flavor of ultra-high-temperature

sterilized milk stored for 100 days at 22 °C. The 5 member taste panel graded intensities of stale and cooked flavors on a 9 point scale (0=none; 9=pronounced).

Dimick (1973) used a 12 member trained panel to judge the effect of fluorescent light on the flavor of homogenized milk held in unprinted fiberboard, blown mold plastic, and clear flint glass containers. Milk samples were graded for preference based on a 9-point hedonic scale (1=dislike extremely; 9=like extremely) and a multiple comparison test using the control sample as reference.

Coleman et al. (1976) organoleptically evaluated pasteurized, homogenized milk samples exposed to fluorescent light. They obtained the preference evaluations using a 9-point hedonic scale (from 1=dislike extremely, to 9=like extremely) and multiple comparison tests (numbers less than 5 indicated dislike, and numbers more than 5 indicated like better than the reference) with the control as reference. Milk samples were judged for flavor deterioration in pasteurized milk packaged in PE-coated cartons and PE-bottles. A hedonic rating scale with eight points of response from 1(dislike extremely) to 8(like extremely), was used for grading the milk samples (Schroder et al., 1985).

Leong et al. (1992) tasted milk packaged in PE-coated paperboard containers to determine the presence or absence of packaging flavor. They used pairwise ranking test to determine the effects of various fat concentrations in milk, storage time, container size, and heat sealing of package.

## **Chapter 1**

### **SENSORY EVALUATION OF MILK PACKAGED IN POLYETHYLENE COATED, PAPERBOARD CONTAINERS**

The objectives of this research were:

1. To survey consumer populations, especially school children, to find the extent of off-flavor perception resulting from the packaging of milk in polyethylene coated, paperboard containers.
2. To survey consumer populations, especially school children, to learn flavor preference for milk based on the type of package used.
3. To study the development of "packaging" flavor in water packaged in the polyethylene coated paperboard containers.

### **MATERIALS and METHODS**

#### **Consumer panel**

##### Sample preparation

Fresh, pasteurized, homogenized, 2% fat milk, packaged in half-pint (236-ml) PE-coated paperboard containers and gallon (3780-ml) blow molded, high density polyethylene



(HDPE) containers, was obtained from a local dairy processor immediately after processing and packaging. Milk ( $2.2^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ) was transported by car in insulated styrofoam containers (approximately 15 minutes), and the HDPE-packaged milk was transferred into clean 4000-ml Pyrex Erlenmeyer flasks (Corning Glass Works, Corning, NY). Temperature in styrofoam containers was maintained using frozen ice-packs. Temperature of the cooler was measured immediately on arriving at the laboratory. Milk was kept in the dark during transport and storage. All milk was then stored in a walk-in refrigerator maintained at  $2.2^{\circ}\text{C} (\pm 2^{\circ}\text{C})$  for three days before samples were prepared to take to the schools for sensory studies.

The milk samples stored in half-pint (236-ml) PE-coated paperboard containers and 4000-ml Pyrex Erlenmeyer flask were removed from the walk-in refrigerator one hour prior to sensory analysis. Milk was transferred from half-pint PE-coated paperboard cartons to a 4000-ml Pyrex Erlenmeyer flask. Both the control, stored in a 4000-ml Pyrex Erlenmeyer flask and cartoned milk samples ( $30\text{ ml} \pm 5\text{ ml}$ ) were dispensed into 2-fl. oz. clear polystyrene containers with lids (Sweetheart® US2 and LUS2, Maryland Cup Corporation, Owing Mills, MA), which had been previously coded with a three-digit random number (Appendix A). The sample codes were changed each time the sensory evaluation was conducted. The milk samples were packed into an electric cooler that was plugged into the car battery, on

way to school to keep the samples at serving temperature.

### Sensory Evaluation

The consumer panel consisted of 181 children from grades one through twelve from the schools in and around the Lansing, Michigan area. The elementary school children accounted for more than seventy five percent of the consumer panel. Permission was obtained in advance from school authorities to conduct the sensory studies. Each child willing to take part in the sensory study was given a consent form to be signed by their parents/guardians. The completed consent forms were collected before the start of the first sensory session. Samples were presented to the children in a randomized and balanced order with two different sets of milk samples during each tasting session. The first set consisted of control and cartoned milk samples, and children were asked to circle the code number of the milk sample they preferred (paired preference test, Appendix B). For the second set, a Hedonic scale (Appendix C) was used, and children were asked to circle the words that best described their feeling for each sample. Each child took part in sensory testing on three separate days.

### Statistical Analysis

For the paired preference test, a two-sided paired comparison test was applied (Meilgaard et al., 1987). Fifty percent of the samples were presented in the ab format and

fifty percent in ba format. The null hypothesis,  $H_0$ : No preference, was tested using the two sided paired comparison table at 10% level of significance (Meilgaard et al., 1987).

For the acceptability test, a nine point Hedonic scale labeled "Super Good" to "Super Bad" was used. The results were tested using the paired t-test at the 10 % level of significance (Meilgaard et al., 1987).

### **Trained panel**

#### Sample Preparation

Gable-top, preformed, empty, half-pint size containers were obtained from three major manufacturers (x, y and z). These cartons were filled with double distilled water using a sterile, disposable 60 cc syringe with a Luer-Lok tip (Becton Dickinson & Company, Rutherford, NJ). The syringe was inserted through the middle of the heat sealed top so that it was positioned in the middle of the gable top carton. Double distilled water packaged in half-pint cartons was compared among themselves and/or to the water stored in a glass container after three day storage at 2.2 °C ( $\pm 2$  °C).

The water samples stored in half-pint (236-ml) PE-coated paperboard containers and 4000-ml Pyrex Erlenmeyer flask were removed from the walk-in refrigerator one hour prior to sensory analysis. Water was transferred from half-pint PE-coated paperboard cartons to a 4000-ml Pyrex Erlenmeyer flask. Both the control, stored in a 4000-ml

Pyrex Erlenmeyer flask and cartoned water samples (30 ml  $\pm$  5 ml) were dispensed into 2-fl. oz. clear polystyrene containers with lids (Sweetheart® US2 and LUS2, Maryland Cup Corporation, Owing Mills, MA), which had been previously coded with a three-digit random number (Appendix D). The sample codes were changed each time the sensory evaluation was conducted. Samples were presented to each judge in a randomized order in a tray with six pairs of water samples and a cup of double distilled water for oral rinsing between samples.

#### Panel Training

Sensory evaluation was carried out to determine if a panel trained to detect "packaging flavor" could differentiate between milk stored in PE-coated paperboard and glass containers. Seventeen subjects participated in four training sessions over a two-week period. The participants were pre-screened for milk consumption habits and interest.

Subjects were tested for their discrimination ability among water samples using a series of two triangle tests (Appendix E) during each training session. The samples used for screening consisted of double distilled water packaged in half-pint cartons and glass container (control), and stored for three days at 2.2 °C ( $\pm$  2 °C). Each panelist was made aware of the objectives of the study before testing commenced. Eleven of the seventeen participants

successfully discriminated among the water samples.

### Sensory Evaluation

The final eleven member trained panel consisted of two faculty and nine students at Michigan State University and included five males and six females between the ages of 20 and 45. Selection criteria included ability to discriminate and to reproduce results, prior tasting experience, availability for tasting, and motivation. Screened subjects were informed of the study objectives and given instructions for evaluating test samples. Subjects were presented with six pairs of samples in a randomized and balanced order. The panelists were asked to identify the sample with a higher degree of packaging flavor (Appendix F). Double distilled water was used for oral rinsing between samples. Judges evaluated the samples in individual, partitioned booths under fluorescent light in a quiet, sensory evaluation laboratory maintained at 22 °C. Tasting sessions were conducted midmorning and usually lasted less than ten minutes. The panel evaluated all samples in triplicate, and the experiment was repeated with three different sets of samples at two different times (Fall and Summer) of the year. All samples were evaluated at 2.2 °C ( $\pm 2$  °C) using paired comparison tests (Meilgaard et al., 1987).

### Statistical Analysis

The pair-wise ranking test with Friedman analysis was used to analyze the data from the trained panel. This test was chosen because several samples were compared for a single attribute, the "packaging flavor". The Friedman approach also arranges the samples on a scale of the intensity of the attribute and provides a numerical indication of the difference between samples and significance of differences. The value of Friedman's T was compared to the critical value of  $\chi^2$  with (t-1) degrees of freedom. When significance was observed (minimum  $\alpha = 0.1$ ) rank sums were compared using Tukey's Honestly Significant Test (HSD) test (Meilgaard, M. et al., 1987).

## **RESULTS AND DISCUSSION**

### **Sensory Studies with School Children**

Two individuals experienced in the flavor quality of fluid milk screened the milk samples that were presented to the school children. They did not find a flavor defect in the control sample but found a typical and definite "packaging flavor" in the sample packaged in cartons.

Nine groups of school children took part in the evaluation of milk packaged in gable-top containers. Three groups (C,D and G) showed a significant preference for milk stored in the glass container (control) versus the milk stored in the gable-top cartons (Figure 1). The rest of the

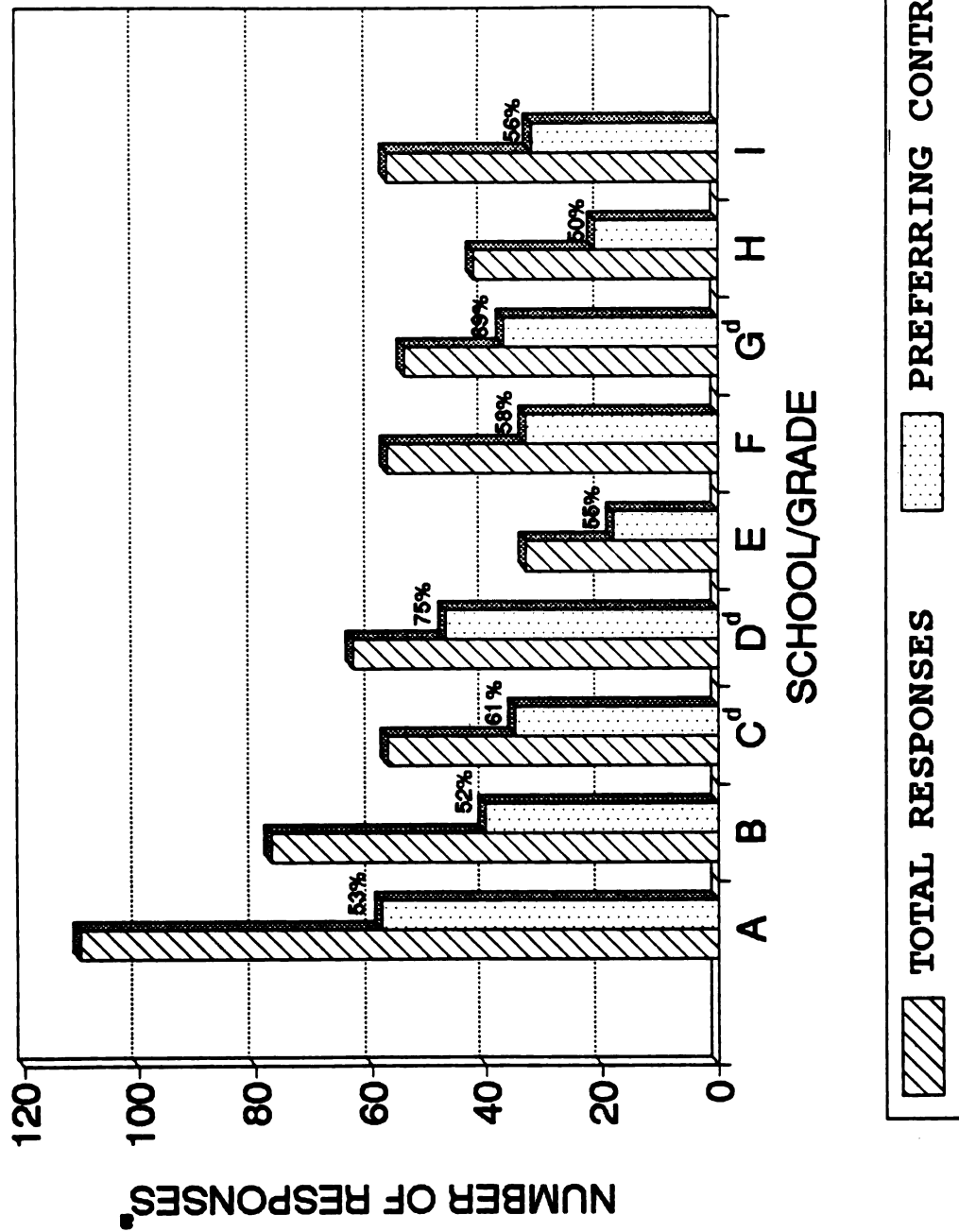


Figure 1. Paired comparison test results for sensory studies of 2% fat milk packaged in glass (control) and half-pint polyethylene coated paperboard cartons after 3 day storage at 2.2 °C by nine groups of school children.

<sup>a</sup> Total of 3 replications; <sup>d</sup>  $p < 0.01$

groups had greater than fifty percent preferring the control milk but the results were not significant at  $p < 0.1$  (Appendix G & H). The data were also analyzed for total number of elementary school children (grades 2nd through 5th). The combined data showed that elementary school children preferred the control versus the milk stored in the gable-top cartons (Figure 2). The results were found significant at  $p < 0.01$ . The result for all school children combined also showed the same result as for elementary school children. Overall, it can be concluded that the school children, especially elementary school children, prefer the milk stored in glass containers versus the milk stored in gable-top cartons. The storage of milk for 3 days at  $2.2^{\circ}\text{C} (\pm 2^{\circ}\text{C})$ , in polyethylene coated paperboard cartons imparted an off-flavor to the packaged milk. This off-flavor was responsible for children preferring milk stored in glass over milk stored in PE-coated paperboard cartons.

The problem of off-flavor development in milk packaged in polyethylene and paperboard containers has been well documented. Our results are in agreement with those found by Bojkow *et al.* (1976), Bojkow *et al.* (1977), Berg (1980), and Leong *et al.* (1992). These studies compared the milk packaged in glass containers with milk stored in PE-coated paperboard cartons. Sensory evaluations indicated that judges preferred the milk stored in glass containers. The milk packaged in PE-coated cartons developed an off-flavor



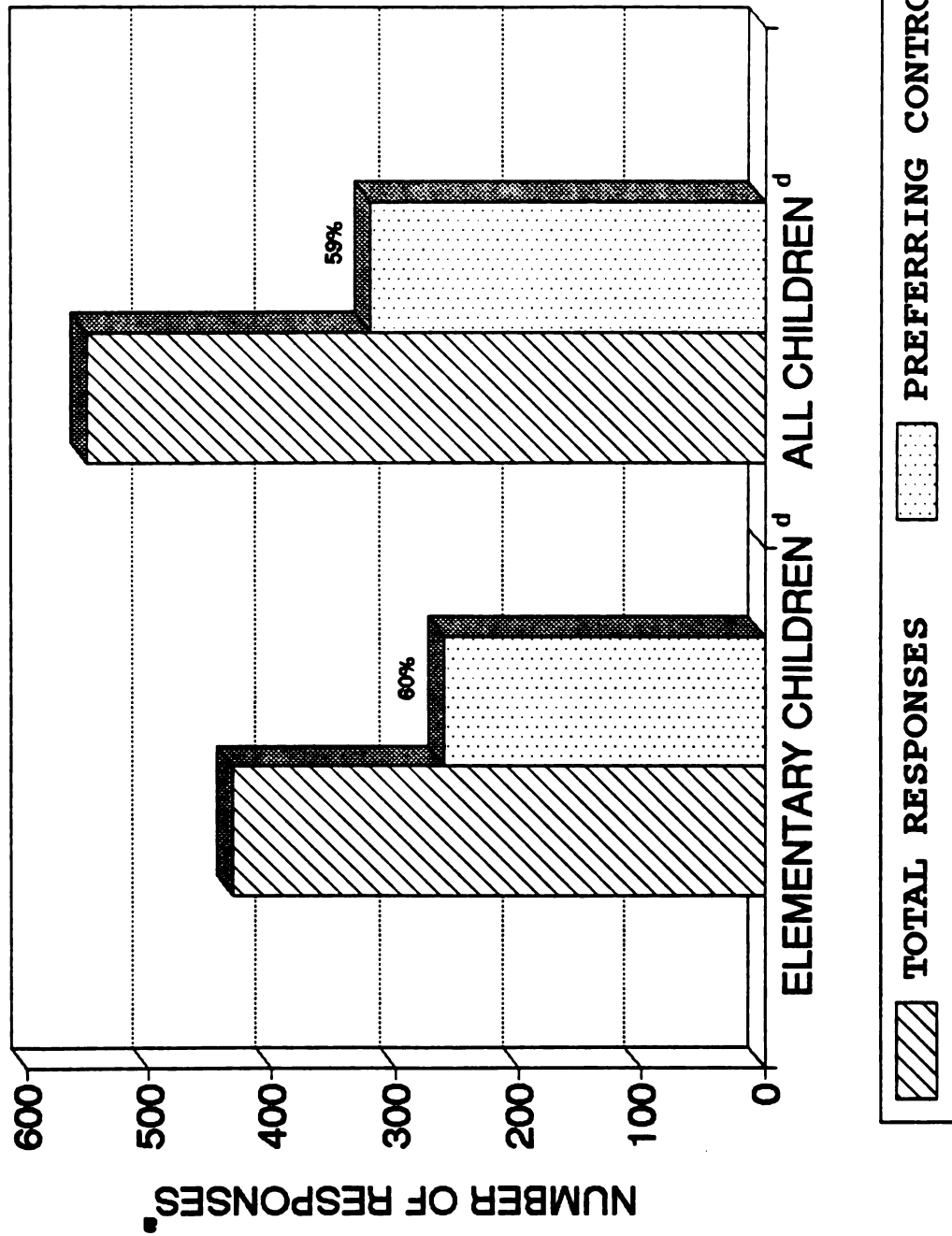


Figure 2. Paired comparison test results for sensory studies of 2% fat milk packaged in glass (control) and half-pint gable-top milk cartons after 3 day storage at 2.2 °C by elementary and total school children population.

<sup>d</sup> Total of 3 replications; <sup>a</sup>  $p < 0.01$

which was characterized as oxidized (Bojkow *et al.*, 1976; Bojkow *et al.*, 1977), off-taste (Berg, 1980), or cardboardy (Leong *et al.*, 1992). This off-flavor development in milk might be due to migration of low molecular weight components from the plastic (Wildbrett, 1968; Chuchlowa and Sikora, 1976), because of surface oxidation of PE (Bojkow *et al.*, 1976), or migration of package components to the stored milk (Leong *et al.*, 1992).

Simon and Hansen (1995) studied the effect of six different packaging boards on the shelf life and flavor of pasteurized milk and reported different results. They reported that all off-flavors detected in milk samples stored for 4 weeks at 5.6 °C, were due to microbial spoilage and the use of different type of packaging boards had no effect on the off-flavor development. This study did not compare the milk stored in the glass container to the milk packaged in different type of packaging boards. Also, the milk samples were stored for 4 weeks before being evaluated, which is not a logical time span between production, packaging and consumption of pasteurized milk.

All groups of school children rated the control milk higher in acceptability than the milk packaged in gable top cartons (Figure 3). All groups except B, E and F, demonstrated a significantly greater acceptability rating ( $p < 0.1$ ). When the data were combined for the elementary school children, the pooled group showed a significantly ( $p < 0.05$ ) higher acceptability for the control milk (Appendix

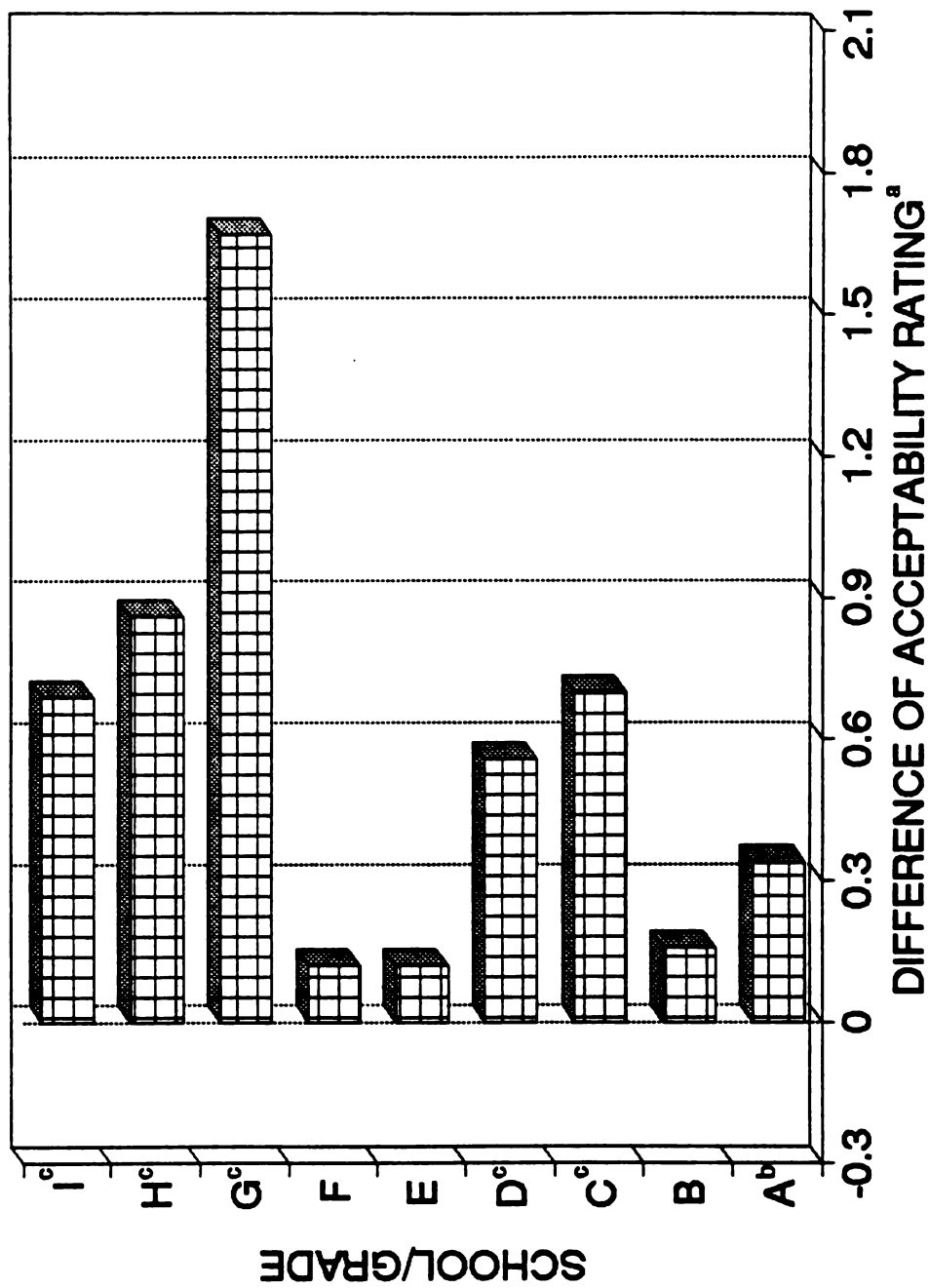


Figure 3. Acceptability test results for sensory studies of 2% fat milk packaged in glass (control) and half-pint polyethylene coated, paperboard cartons after 3 day storage at 2.2 °C by nine groups of school children. Positive value for difference of acceptability rating shows children in that group preferred control milk over cartoned milk. <sup>a</sup> Total of 3 replications; <sup>b</sup>  $p < 0.1$ ; <sup>c</sup>  $p < 0.05$

G & I). Similar results were observed, when the data for all the school children were pooled together (Figure 4). These data support our hypothesis that milk packaged in PE-coated, paperboard containers develop off-flavors perceived by consumers, here, school children. Bandler *et al.*, (1975) reported a direct correlation between the flavor and consumption of milk by school age children. They observed a high incidence of off-flavor in a survey of 693 schools in New York State. It was found that the schools where milk tasted good (38-40 flavor score) the average milk consumption was 90.4%. Where the flavor score was 37 or less the average consumption was 66%. This spread between good and poor tasting milk showed that flavor was a major factor in the acceptance of white milk in schools.

#### **Sensory Studies with Trained Panel**

The data from the trained panel were analyzed (Appendix J) using the Friedman analysis (Meilgaard, M. *et al.*, 1987). The critical T value of 11.3 ( $p < 0.01$ ) was less than the calculated value of 41.65 (Figure 5). This showed that a significant difference existed among the four samples ( $p < 0.01$ ).

The Honestly Significant Difference (HSD) value was used to compare the rank sums (Figure 5). The difference between g and x; g and y; g and z; x and y; and x and z was bigger than HSD of 29.49 (Appendix J). However, the difference between y and z was smaller than HSD of 29.49.

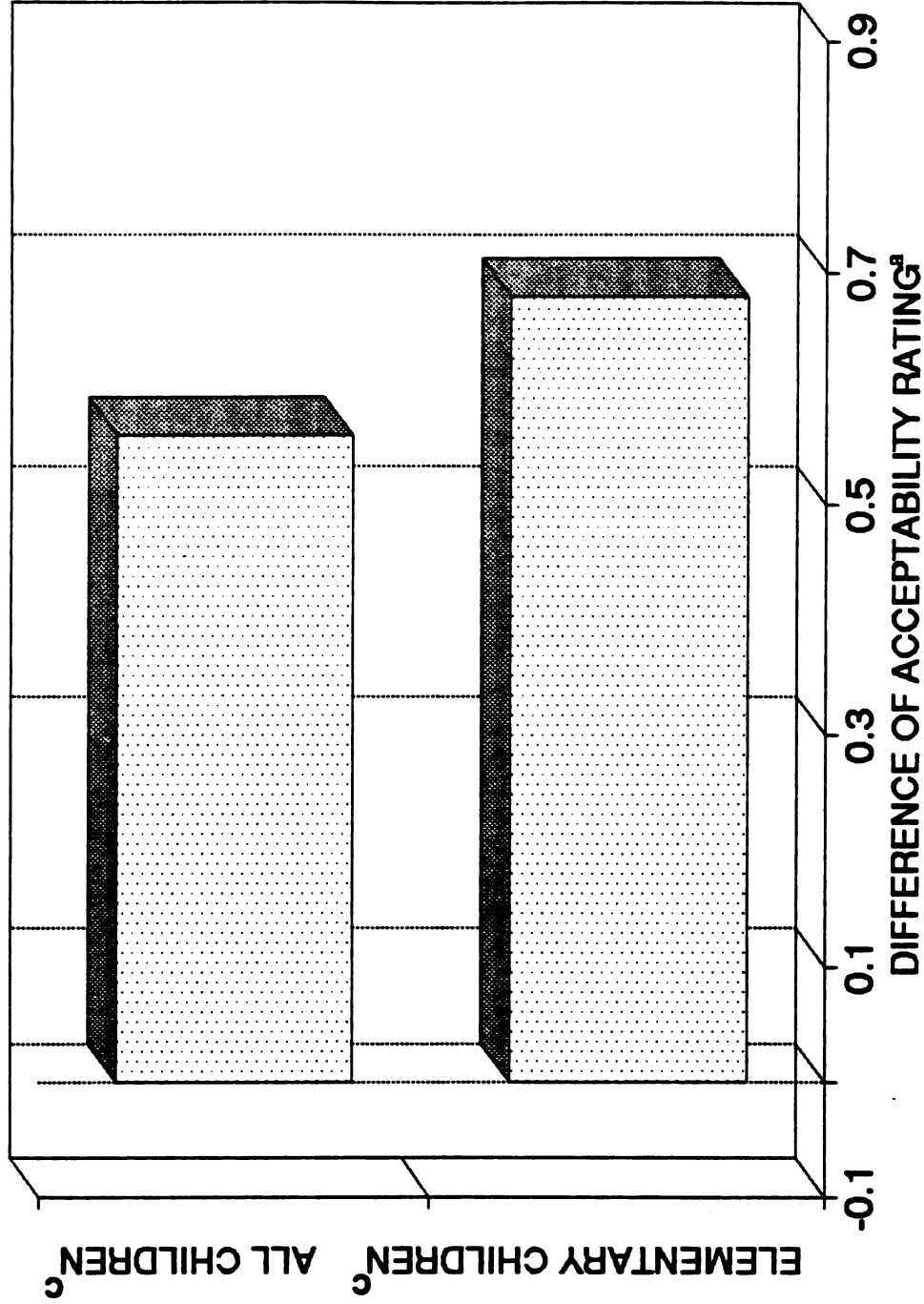


Figure 4. Acceptability test results for sensory studies of 2% fat milk packaged in glass (control) and half-pint polyethylene coated, paperboard cartons after 3 day storage at 2.2 °C by elementary and total school children population. Positive value for difference of acceptability rating shows children in that group preferred control milk over cartoned milk. Total of 3 replications;  $p < 0.05$

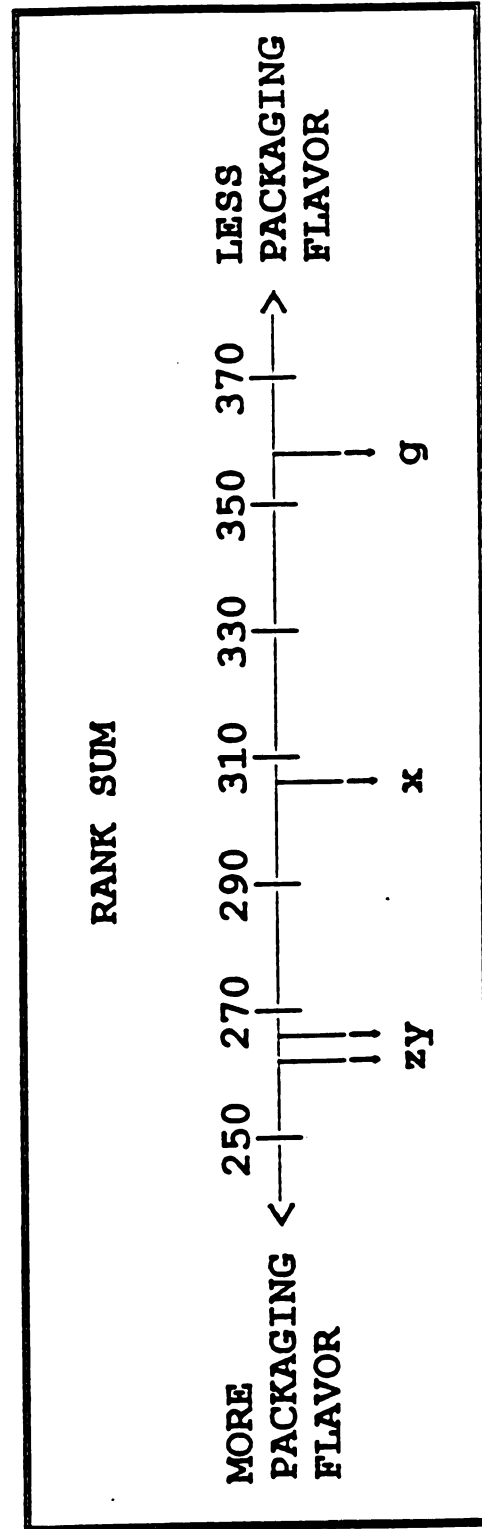


Figure 5. Rank sums obtained for the water samples using the sensory data from the trained panel. "x", "y" and "z" are the rank sums for water samples stored in polyethylene coated paperboard containers from the three manufacturers and "g" is rank sum for water sample stored in glass container.

The results indicated that the water samples stored in PE-coated paperboard cartons showed a significant ( $p < 0.1$ ) presence of the "packaging flavor", which was absent in the water packaged in glass containers. Samples y and z had more packaging flavor ( $p < 0.1$ ) than x, however, sample y did not differ significantly ( $p < 0.1$ ) from z. Milk cartons from the three manufacturers contributed different levels of "packaging flavor", to the stored water, but they all showed higher levels ( $p < 0.1$ ) of "packaging flavor", than the water stored in a glass container.

Ideal food packaging should be inert to the packaged food and therefore should not contribute any kind of flavor to it. The presence of "packaging flavor" in milk packaged in PE-coated containers indicate the problem of migration of certain unwanted flavor compounds from the packaging to milk. This never resulted when the milk was exclusively packaged in glass containers.

Leong et al. (1992) and Berg (1980) observed similar results for milk and water samples stored in glass and PE-coated paperboard containers. The milk and water stored in PE-coated paperboard containers showed a significantly higher level of off-flavor than the samples stored in glass containers. This off-flavor was not due to storage temperature, lipid oxidation or excessively high heat sealing temperatures.

### CONCLUSIONS

Packaging flavor developed in milk and water packaged in half-pint PE-coated cartons after three days of storage. Sensory studies with school children showed results significant enough to state that children preferred the milk stored in the glass containers over the milk stored in PE-coated paperboard containers. Also, this problem was confirmed by the results obtained from the study with the trained panel. Every time an off-flavor is detected in a food product, every effort should be made to correct the problem. Here, the presence of off-flavor is more critical as this may result in a negative impact on school childrens' attitude toward consumption of milk.



## **Chapter 2**

### **IDENTIFICATION OF OFF-FLAVOR COMPONENTS FOUND IN MILK PACKAGED IN GABLE-TOP, PAPERBOARD CONTAINERS**

#### **INTRODUCTION**

Fresh, pasteurized milk contained in polyethylene coated cartons presented an undesirable off-flavor, which had never been indicated when milk was exclusively packaged in glass bottles (Bojkow *et al.*, 1976; Bojkow *et al.*, 1977; Berg, 1980; Leong *et al.*, 1992). This off-flavor has been described as "strange" (Bojkow *et al.*, 1977); "unpleasant plastic" (Berg, 1980) or "cardboardy " (Leong *et al.*, 1992). The incidence of off-flavor in milk packaged in milk cartons necessitates the need for research into potential interactions that might arise between milk and packages and the effects that these might have on milk quality.

The objectives of this study were:

1. To develop a technique to isolate the volatile compounds migrating from milk cartons to the enclosed product.

2. To identify the off-flavor components which contribute to the packaging flavor detected in milk packaged in PE-coated paperboard containers.

## **MATERIALS AND METHODS**

### **Sample Preparation and Analysis using Thermal Desorption**

A dynamic headspace analysis method was used to examine for presence of compounds responsible for the "packaging flavor" in water packaged in PE-coated paperboard containers. In order to maintain the fairness of the study, the Gable-top, preformed, empty, half-pint size containers were obtained from the three major manufacturers (x,y & z). Some of the specifications for these cartons are listed in Table 1. HPLC grade water (Fisher Scientific, Fair Lawn, NJ) was introduced into the preformed cartons using a sterile, disposable 60 cc syringe with a Luer-Lok tip (Becton Dickinson & Company, Rutherford, NJ). The needle was inserted through the middle of the heat sealed top so that it was positioned in the middle of the gable top carton. The water samples were analyzed after three days of storage at  $2.2^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . Carton materials obtained from x, y & z manufacturers were analyzed for the presence of "packaging flavor" volatiles that may migrate into the water samples. Also, polyethylene beads and the paperboard stock obtained from one of the manufacturers were analyzed.

Table 1. Specifications of the half-pint polyethylene coated paperboard cartons obtained from 3 manufacturers (x, y & Z).

Property (unit)	Sample x	Sample y	Sample z
Basis weight (lbs./3,000 sq.ft.)	183	170	172
Caliper (inch)	0.0156	0.0174	0.0168
Caliper of base stock (inch)	0.0143	0.0163	0.0158
Outside resin film weight (lbs./3,000 sq.ft.)	10	8	8
Inside resin film weight (lbs./3,000 sq.ft.)	16	15	14
Surface area (cm <sup>2</sup> ) <sup>a</sup>	186.20	198.93	198.93

<sup>a</sup> Calculations for surface area are shown in Appendix K

#### Purge and trap apparatus

A purge and trap system was designed for dynamic headspace sampling of the aqueous and solid samples. A 100 mm Wheaton dry sealing desiccator with lid was modified to serve as the glass trapping apparatus, to collect volatiles from both solid (cartons, paperboard and PE) and aqueous (water) samples. The modification of the dry sealing desiccator was performed by the Chemistry Department Glass Blowing Shop at Michigan State University. A schematic diagram of the purge and trap system is shown in Figure 6. The desiccator was ordered with two lids. One of the lids was fitted with a dispersion tube assembly to allow the bubbling of the nitrogen gas through the aqueous samples. The second lid was used during the analyses of solid samples.

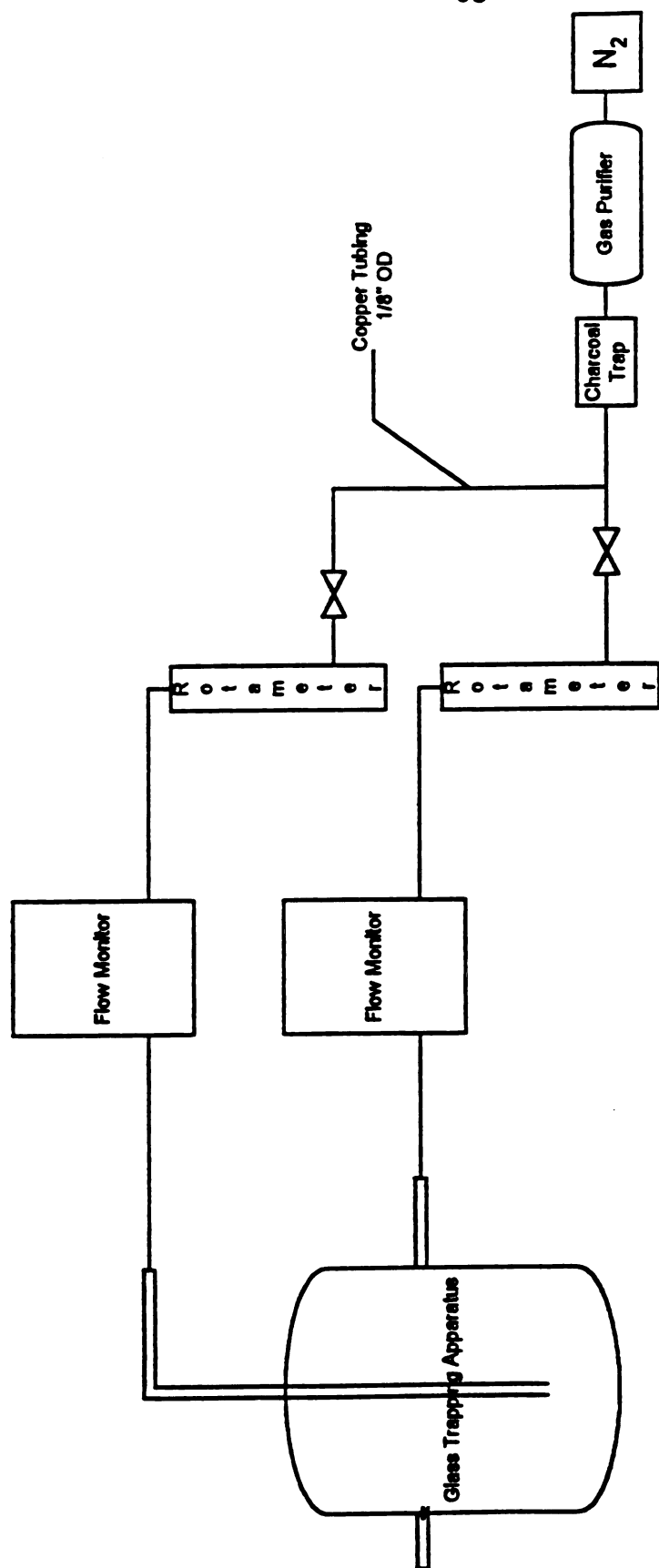


Figure 6. Purge and trap glass trapping apparatus for thermal desorption and gas chromatography studies.

A cylinder of compressed nitrogen was interfaced to a dispersing manifold through a gas purifier (Supelco Inc., Bellefonte, PA) and a charcoal trap (Supelco Inc., Bellefonte, PA). The dispersing manifold consisted of two flow meters and needle valves, all connections were through 1/8" O.D. copper tubing and swagelok fittings. Flow meters were used to provide a continuous indication that a constant nitrogen flow rate was maintained to the purge and trap cell.

The trapping system was designed to ensure that the sample was continuously flushed with nitrogen gas and the desorbed volatiles conveyed to the trapping tube attached. The sorption trap was connected to the exit port of the desiccator via swagelok adapters. The dispersion head exit port of 1/4" O.D. glass tubing was connected by a 1/4" swagelok nut and an adapter to a 1/4" male swagelok fitting. The sorption trap was mounted to the dispersion head with a 1/4" thumb wheel swagelok fitting (Supelco Inc., Bellefonte, PA) for easy removal.

#### Sample preparation

To establish optimum procedure conditions for the analysis of sorbed off-flavor volatiles in the product samples, several temperature/time combinations were evaluated in a series of preliminary runs. A purge time of 24 hours at 40 °C under 100 ml/min flow of nitrogen and a purge time of 5 hours at 40 °C under 25 ml/min flow of

nitrogen provided chromatograms which showed good peak resolution for solid and aqueous samples, respectively. Half-pint (236 ml) of water and 11 cm diameter solid sample cut out of a knocked-down carton served as the standard sample amounts for aqueous and solid samples, respectively.

Prepacked adsorbent tubes (Carbotrap<sup>TM</sup> 300) were bought 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 20/40 mesh Carbotrap C (300 mg), 20/40 mesh Carbotrap B (200 mg), and 60/80 mesh Carboseive S-111 (125 mg). Before each use, tubes were conditioned at 370 °C for 90 minutes in the sample preparation path of the thermal desorption unit. After sample collection, the adsorbent tubes were sealed and stored in a refrigerator.

#### Thermal desorption and gas chromatographic analysis

Volatiles were desorbed from sample tubes on a thermal desorption unit (Model 890, 110 VAC, Dynatherm Analytical Instruments, Inc., Kelton, PA) which was connected to a gas chromatograph (Model 5890A, Hewlett-Packard, Chicago, IL) equipped with a flame ionization detector. The conditions used for the thermal desorption of the samples were:

Desorption temperature:	350°C
Desorption time:	4 min
Preparation temperature:	370°C
Preparation time:	90 min
Valve temperature:	230°C

Transfer line temperature: 230°C  
Helium flow for desorption: 5 ml/min  
Helium flow for preparation: 25 ml/min

The thermal desorption unit was connected to the GC by a fused silica transfer line (Supelco Inc., Bellefonte, PA), which was connected to the column by a butt-connector (Supelco Inc., Bellefonte, PA).

The following conditions were found to give best separation during a chromatography run:

Column used: 60 m x 0.32 mm ID fused silica  
capillary intermediate polar  
bonded stationary phase SPB-20  
of 0.25 $\mu$ m film thickness  
(Supelcowax-10, Supelco Inc.,  
Bellefonte).

Initial temperature: 40°C  
Initial time: 10 min  
Temperature rate: 2°C/min  
Final temperature: 165°C  
Final time: 10 min  
Carrier gas flow: 1 ml/min  
Makeup gas flow: 19 ml/min  
Air flow rate: 400 ml/min  
Hydrogen flow rate: 30 ml/min  
Detector temperature: 270°C

The following samples were analyzed using the thermal desorption method:

1. Un-printed, knocked-down milk carton (half pint)
2. Printed, knocked-down milk carton (half pint)
3. Paperboard stock used to manufacture cartons
4. Water stored in formed milk carton (half pint)
5. Water stored in glass container

*Due to insurmountable difficulties with the interfacing of the thermal desorption unit and the mass selective detector (MSD), a second analytical protocol was developed to enable identification of potential off-flavor components.*

#### **Sample Preparation and Analysis using Solvent Extraction**

##### **Preparation of adsorbent traps**

Empty metal tubes (4 mm ID and 11 cm long) with capped ends were obtained from Scientific Instrument Service, Inc. (Ringoes, NJ) and 0.17 g of 60/80 mesh Tenax-GC (Alltech Associates, Inc., Deerfield, IL) was packed using silicanized glass wool (Supelco Inc., Bellefonte, PA) plugs at both ends to hold the adsorbent in place. The traps were conditioned at 200°C for 36 hours, with 25 ml/minute of nitrogen flowing through. The traps were cooled, rinsed with 2 ml of hexane (J. T. Baker Inc., Phillipsburg, NJ) to clean any residual contaminants, and allowed to dry in a desiccator for one hour prior to use. All samples were



purged for 24 hours under 25 ml/min flow of nitrogen. The temperature was maintained at 40°C during sample collection.

HPLC grade water (Fisher Scientific, Fair Lawn, NJ) was stored in preformed cartons obtained from the three major manufacturers (x, y & z). The water was injected into the cartons as described for the analysis by thermal desorption technique.

#### Purge and trap apparatus

A dynamic gas purge and trap system was designed for dynamic headspace sampling of the water samples. Three 500 ml twin necked round bottom flasks were fitted with the modified version of dispersion tube assembly of a gas washing bottle (Stopper assemblies for Corning 31770 gas washing bottles, Fisher Scientific, Pittsburgh, PA). The modification of the dispersion tube assembly of the gas washing assembly was performed by the Chemistry Department Glass Blowing Shop at MSU. A schematic diagram of the dynamic purge and trap system is shown in Figure 7. A cylinder of compressed nitrogen was interfaced to a dispersing manifold which consisted of three flow meters and needle valves, all connections were through 1/8" O.D. copper tubing and swagelok fitting. Flow meters were used to provide a continuous indication that a constant rate of flow of nitrogen was maintained to the individual purge and trap cells.

The trapping system was designed to ensure that the

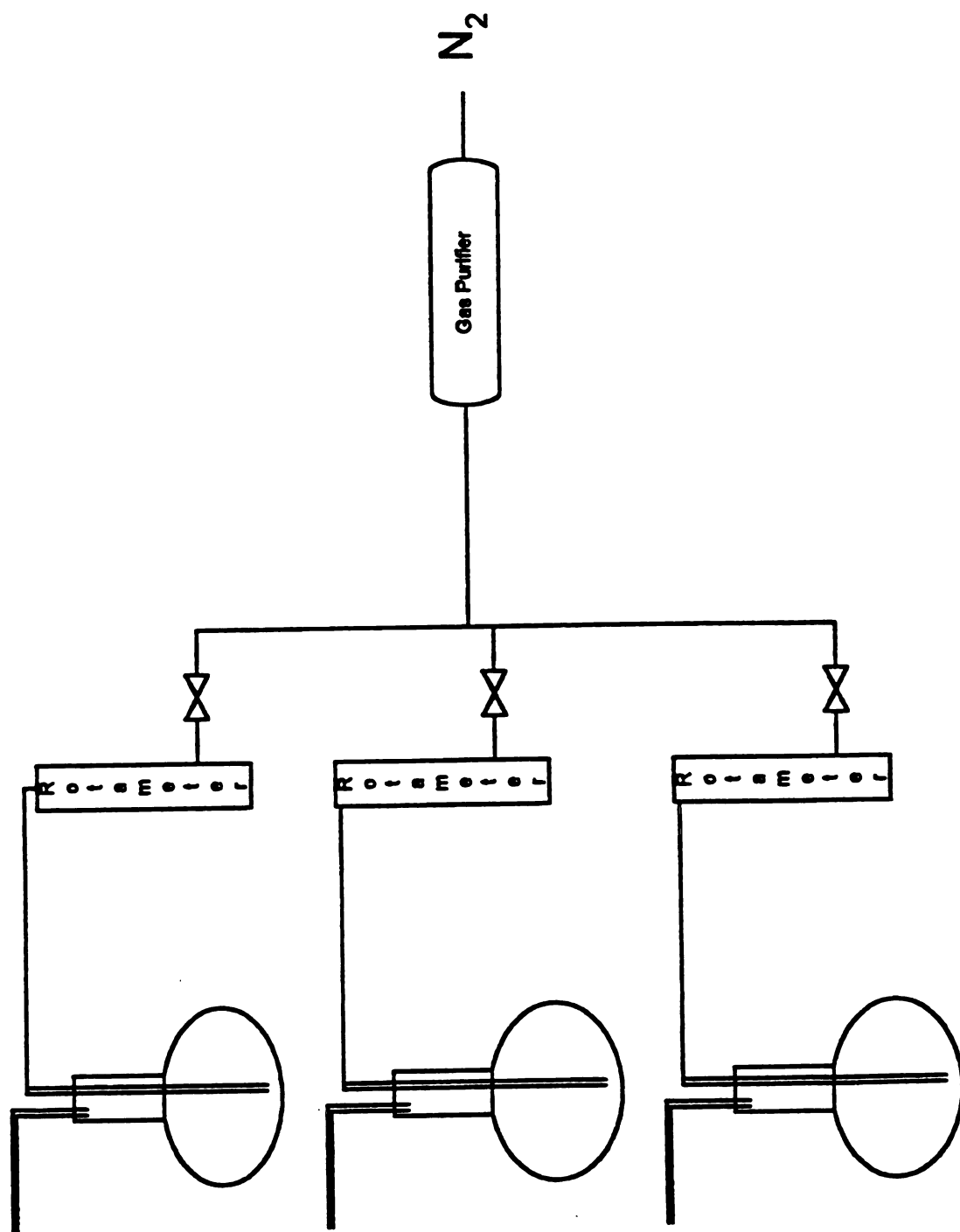


Figure 7. Purge and trap glass trapping apparatus for solvent extraction, gas chromatography and mass spectrometry studies.

sample was continuously flushed with nitrogen gas and the desorbed volatiles conveyed to the trapping tube attached. The sorption trap was connected to the exit port of the dispersion head via swagelok adapters. The dispersion head exit port of 8 mm O.D. glass tubing was connected by a 5/16" swagelok nut and a series of reducing adapters to a 1/4" male swagelok fitting. The sorption trap was mounted to the dispersion head with a 1/4" thumb wheel swagelok fitting (Supelco Inc., Bellefonte, PA) for easy removal.

#### Sample preparation

To establish optimum procedure conditions for the analysis of sorbed off-flavor volatiles in the product samples, several temperature/time combinations were evaluated in a series of preliminary runs. A purge time of 24 hours at 40 °C under 25 ml/min flow of nitrogen provided chromatograms which showed good peak resolution for both solid and aqueous samples.

One half-pint (236 ml) of water served as the standard sample amount. The samples collected were extracted with 2 ml of hexane. The adsorbent tubes were fitted into 15 ml graduated centrifuge tubes (Baxter Scientific Products, McGaw Park, IL) using a cork. Small amounts of hexane were pipetted into the top of the adsorbent tube and the apparatus was centrifuged in a IEC clinical centrifuge (Damon/IEC Division, Needham Heights, Mass.) at 1000 rpm/2 minutes. The procedure was repeated until 2 ml hexane

extract were collected in the centrifuge tube. The extraction step was carried out in the direction opposite to that of sample collection. The hexane extract was further concentrated to 0.1 ml using nitrogen sparging, taking care not to use excessive amounts of nitrogen to avoid loss of volatiles by splashing. The concentrated sample was transferred to an amber colored crimp and seal glass vial (Supelco Inc., Supelco Park, Bellefonte, PA). One microliter of sample was injected for analysis by GC or GC-MSD.

#### Gas chromatographic and mass spectroscopic analysis

The following conditions were found to give best separation during gas chromatography:

Column used:	30 m x 0.25 mm ID DB-5 capillary column with 0.25 $\mu$ m film (J & W Scientific, Folsom, CA).
Initial temperature:	35°C
Initial time:	10 min
Temperature rate (level 1):	2°C/min
Final temperature (level 1):	80°C
Final time (level 1):	0 min
Temperature rate (level 2):	4°C/min
Final temperature (level 2):	280°C
Final time (level 2):	20 min
Carrier gas flow:	1 ml/min

Makeup gas flow:	19 ml/min
Air flow rate:	400 ml/min
Hydrogen flow rate:	30 ml/min
Injector temperature:	270°C
Detector temperature:	270°C

When the gas chromatograph was used in conjunction with the mass selective detector, the following conditions were used for the mass selective detector:

Transfer line temperature:	270°C
Mass scanned:	35 to 450
Purge off time:	4 min

#### **Percent Recovery of Off-flavor Compounds from Tenax and Concentration Technique**

A recovery study was done to determine the percentage of off-flavor compounds that were recoverable from the extraction and concentration procedure. Two solutions of different strengths (40 ppm and 100 ppm) of the standard compound were made in hexane and tested in duplicate to determine the percent recoverable.

A 1 ul aliquot of each solution was injected into the programmed GC in duplicate. An average area response was used as a basis for hundred percent recovery. One ml of each solution was injected into a freshly conditioned metal trap packed with Tenax-GC. Then the extraction and concentration procedure as described previously was followed. A one ul aliquot of each extract was injected

into the programmed GC. The GC conditions used were changed for each standard in order to hasten the process of elution of the desired peak. Injections were done in duplicate. The area responses of the two injections for each extract were averaged. The averages were divided by the area response set as a basis for 100% recovery for that solution to determine the % recovery using this technique.

#### **Percent Recovery of Off-flavor Compounds from Purge and Trap, Tenax and Concentration Technique**

A recovery study was done to determine the percentage of off-flavor compounds that were recoverable from the purge and trap, extraction and concentration procedure. Two different strength (40 ppm and 100 ppm) solutions of the standard compound were made in hexane and tested in duplicate to determine the percent recoverable.

One microliter aliquot of each solution was injected into programmed GC in duplicate. An average area response was used as a basis for hundred percent recovery. One milliliter of each solution was transferred to P&T apparatus and purged with nitrogen. The volatiles were collected in the pre-conditioned Tenax-GC trap. The extraction and concentration of volatiles from the Tenax trap was done as discussed before. A one ml aliquot of each extract was injected into the programmed GC. The GC conditions used were changed for each standard in order to hasten the process of elution of the desired peak. The injections were

done in duplicate. The area responses of the two injections for each extract were averaged. The averages were divided by the area response set as a basis for 100% recovery for that solution to determine the % recovery using this technique.

#### **Calibration Curve Development Procedure**

Standards used for the calibration curve consisted of solutions made by dissolving known amounts of nonane (density 0.72 g/ml), 2,6-di-tert-butyl-p-cresol and di[-2-ethyl-hexyl]phthalate (density 0.981 g/ml) in HPLC grade water. Pure standards were obtained from the Sigma Chemical Co. (St. Louis, MO). Volumetric flasks used for the procedure were washed, rinsed with double distilled water and dried in a conditioned 100 °C air oven. While flasks were dried, purity of the standards was tested using the GC. GC conditions were programmed to match those used to run unknowns.

After one hour in the oven, flasks were taken out and cooled to room temperature, at which time the flasks could be labeled with their appropriate concentrations. The standard solutions of known concentration were made for each standard according to procedure listed in Appendix L.

One half-pint (236 ml) of each known standard solution was put in the purge and trap apparatus and purged with nitrogen gas for 24 hours. The volatiles were collected in the pre-conditioned Tenax trap, as explained previously.

The sample was extracted with hexane and concentrated to 0.1 ml using nitrogen as the sparging gas. Two 1 ul injections from each prepared sample were made into the GCMS, using the same syringe (10 microliter syringe from Hamilton Company, Reno, Nevada) for all the injections. After each injection the syringe was washed with hexane and acetone, and heated in a 100 °C oven for 10 minutes to remove all traces of solvent. The results from the two injections at each concentration were averaged and values plotted.

## RESULTS AND DISCUSSION

### Thermal Desorption

Figure 8 shows the gas chromatograms obtained from analysis of half pint un-printed, knocked-down milk carton and the paperboard stock used in the manufacture of the same cartons (x). Paperboard stock was supplied by only one manufacturer, therefore this comparison was not run on samples "y" and "z". Comparison of the two chromatograms indicated the presence of peaks with the same retention times, indicating the possibility of volatiles permeating the polyethylene coating of the carton. Paperboard samples showed peaks which were not present in carton sample. These may be volatiles which were not able to permeate the polyethylene coating on cartons. Hansen *et al.* (1974) reported that UHT milk packaged in a PE bag and cardboard box showed noticeable flavor absorption after 16 days. They



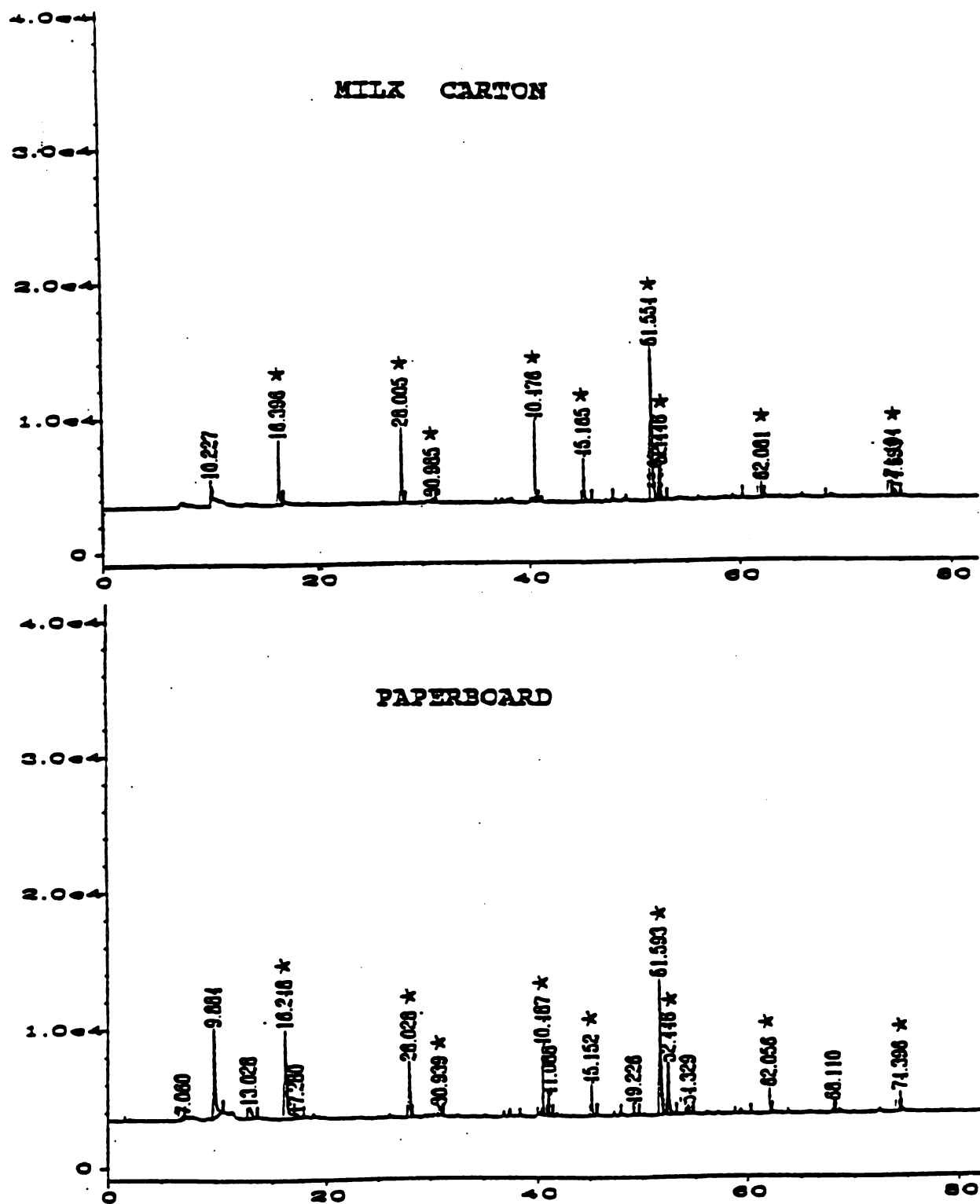


Figure 8. Chromatograms of volatile compounds found in unprinted half-pint polyethylene coated, knocked down cartons from manufacturer "x" and the paperboard stock used in construction of cartons "x" using thermal desorption and gas chromatography.

★ = matching peaks

suggested that possibly the sizing glues and components in the cardboard were absorbed through the PE film.

Figure 9 shows the chromatograms obtained from analysis of un-printed, knocked-down milk cartons and of a water sample stored in formed carton from the same manufacturer (y) and lot. Comparison showed the presence of common peaks in the two chromatograms, indicating that volatiles were migrating from the packaging materials into the water sample stored in the cartons. These compounds may be responsible for the packaging flavor experienced by sensory panels in the stored milk. Also, the water showed peaks not identified in chromatograms from the un-printed, knocked-down milk cartons. These peaks may be due to interaction of water sample with the packaging, and may also be contributing to the packaging flavor. The compounds migrating from the carton to the enclosed water were present in widely different concentrations even in the successive cartons obtained from the same shipping box. Analysis, of samples "x" & "z" showed similar results.

The compounds migrating from the packaging to the enclosed water can be contributed by polyethylene coating (Wildbrett, 1968; Kiermer and Stroh, 1969; Bojkow et al., 1979; Srivastava and Rawat, 1978; Berg, 1980), paperboard (Hansen et al., 1974), and pigments or printing inks (Bojkow et al., 1976; Berg, 1980) used in the manufacture of milk cartons. Bojkow et al. (1979) found that the flavor components migrating from the internal PE coating of the

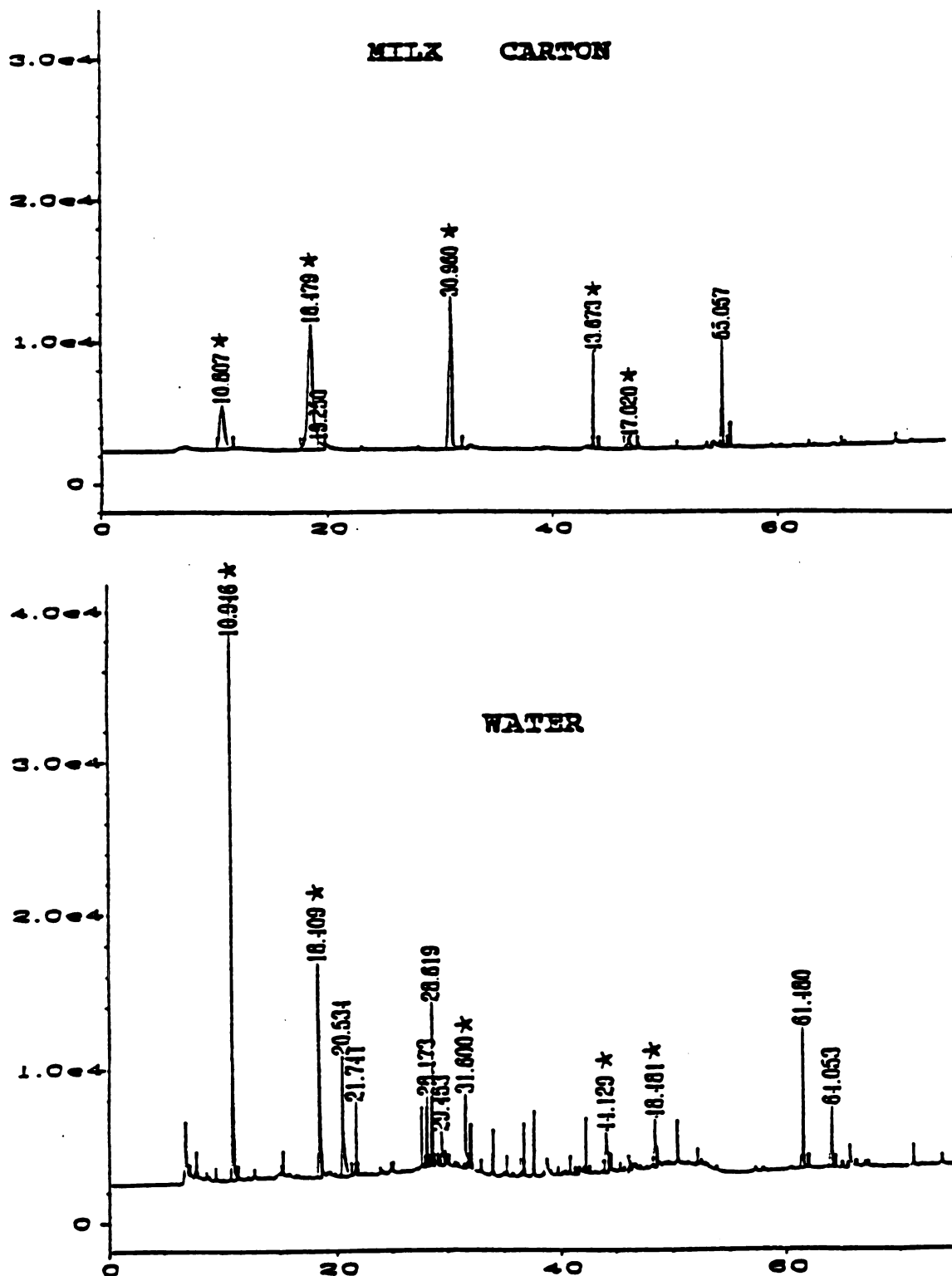


Figure 9. Chromatograms of volatile compounds found in unprinted half-pint polyethylene coated, knocked down cartons from manufacturer "y" and the water stored in preformed, unprinted half-pint cartons from the manufacturer "y" using thermal desorption and gas chromatography.

★ = matching peaks

package were largely soluble in water and quite volatile. Even in successive sections of a continuously processed sheeting of packaging material or in successive blanks within a shipping box these components were present in widely different concentrations.

The chromatograms obtained from the water samples stored in the cartons obtained from the three manufacturers (x, y & z) are shown in Figure 10. Peaks found in the water samples stored in cartons were not detectable in the chromatogram from water samples stored in the glass container. The number and intensities of peaks in the chromatogram from sample "x" were found to be less than for samples "y" and "z". Thus the samples "x" should exhibit less off-flavor, as compared to "y" and "z". This was supported by our sensory data in Figure 5, where we did not find any significant difference between samples "y" and "z", but they were both significantly higher in off-flavor than sample "x". The water samples stored in the glass containers did not show many peaks supporting the absence of the off-flavor in these samples. The migration of compounds from the packaging material into the water caused a detectable packaging flavor in the water samples.

Figure 11 shows the chromatograms obtained from analysis of samples from different sections (side panel with and without heat seal, base or top) of half pint un-printed, knocked down milk cartons (z). Comparison of the four chromatograms indicated the presence of same number of peaks

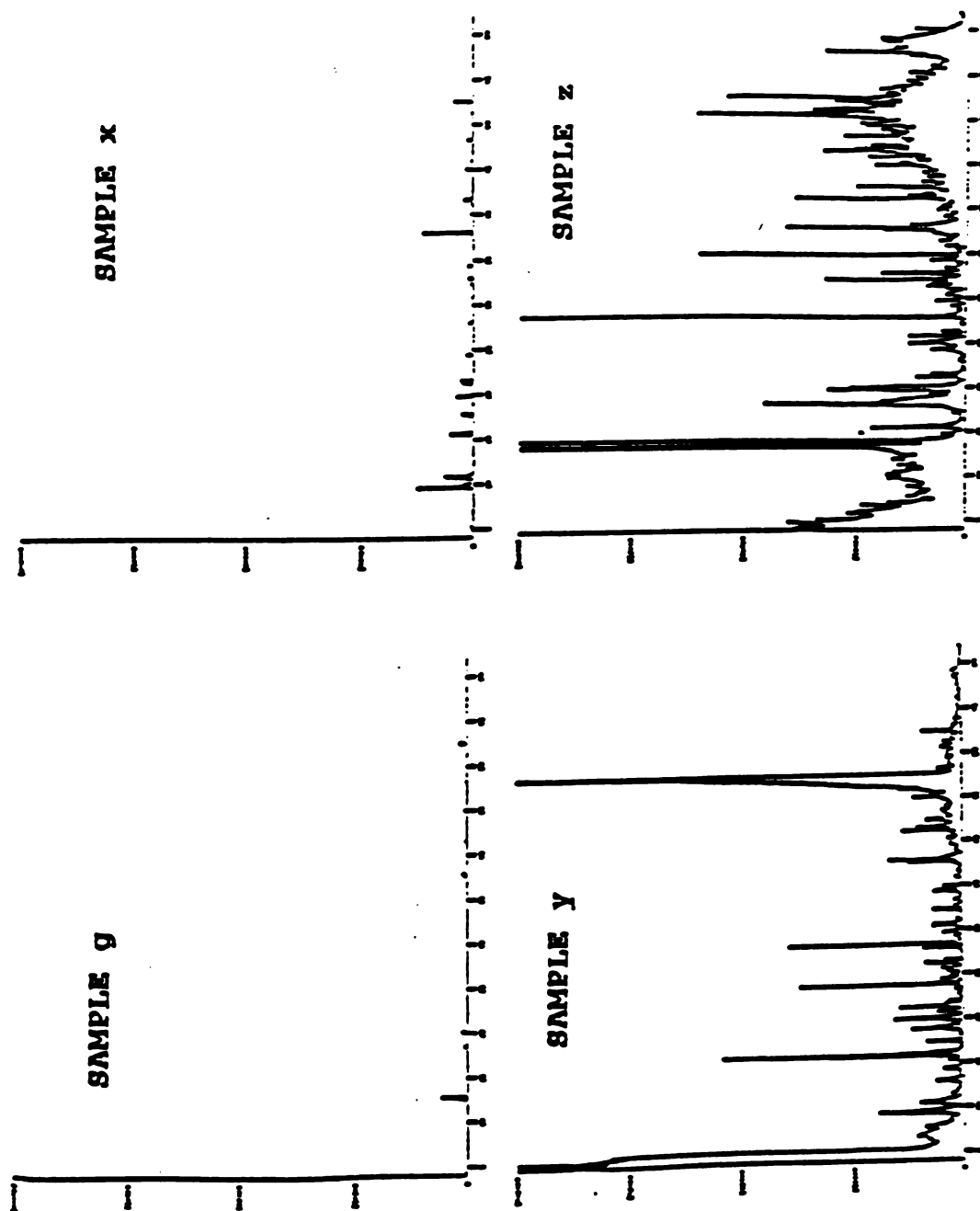


Figure 10. Chromatograms of volatile compounds found in water stored in unprinted half-pint polyethylene coated paperboard containers from the three (x, y & z) manufacturers and water stored in a glass container (g) using thermal desorption and gas chromatography.

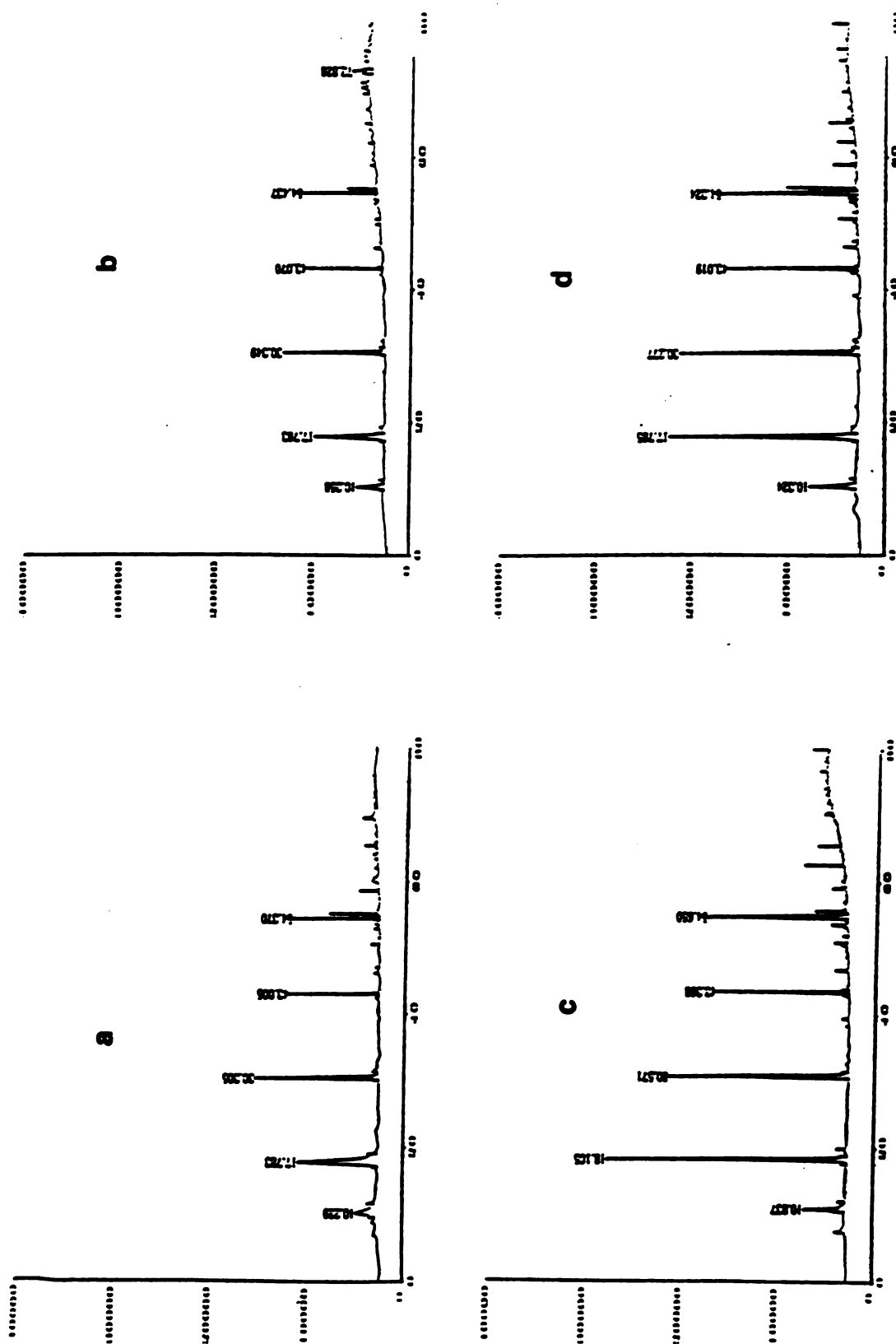


Figure 11. Chromatograms of volatile compounds found in a) top, b) base, c) side panel with heat seal, and d) side panel without heat seal from the knocked-down, unprinted half-pint polyethylene coated, cartons from manufacturer "2".

which eluted out at similar retention times. All sections (side panel with and without heat seal, base or top) of milk cartons contribute equally to the packaging flavor. Analysis of various sections of milk cartons from manufacturer "x" & "y" also resulted in similar chromatograms indicating their equal contribution to packaging flavor.

The chromatogram from analysis of half pint printed, knocked-down milk carton (y) showed peaks which were similar to those present in the half pint un-printed, knocked-down carton (Figure 12). However, the intensities of peaks detected was higher in chromatogram from printed carton. Figure 13 shows the chromatograms obtained from the water samples stored in the half pint printed and un-printed cartons from the same manufacturer (y). The printed carton sample showed some peaks not identified in the chromatogram from un-printed carton. The volatile compounds migrated from the printing ink into the water sample. These migrating compounds may contribute to the packaging flavor. Cartons from manufacturer "x" and "z" lead to similar observations. Bojkow *et al.* (1979) detected the presence of Platinol AH, an additive in coloring matters or printing colors in the inner layer of PE-films and PE-coated papers used in milk packaging. Berg (1980) identified volatile ketones and esters, which might have come from the printing inks used to print the milk cartons.

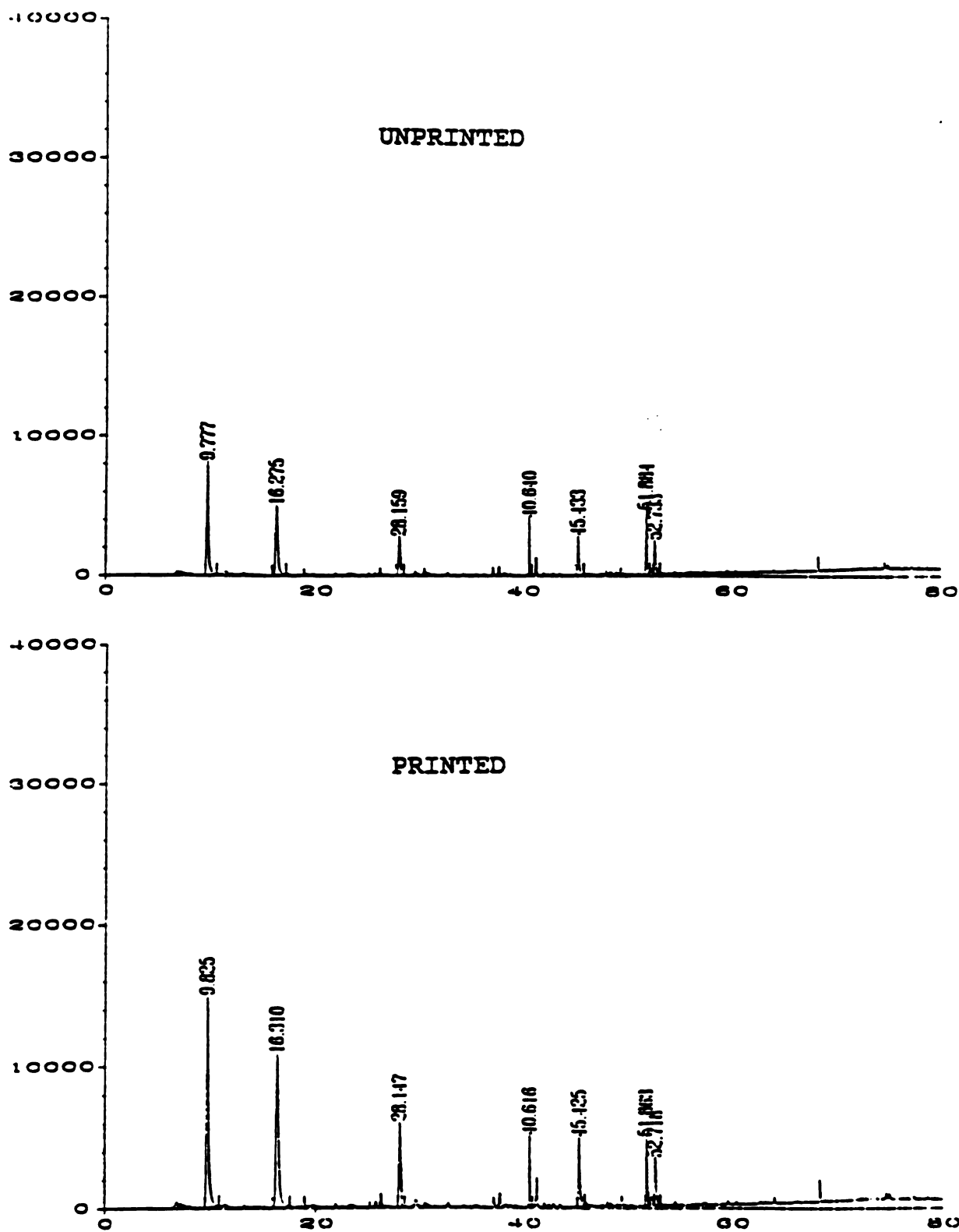


Figure 12. Chromatograms of volatile compounds found in Unprinted and printed half-pint polyethylene coated, knocked down cartons from manufacturer "y".



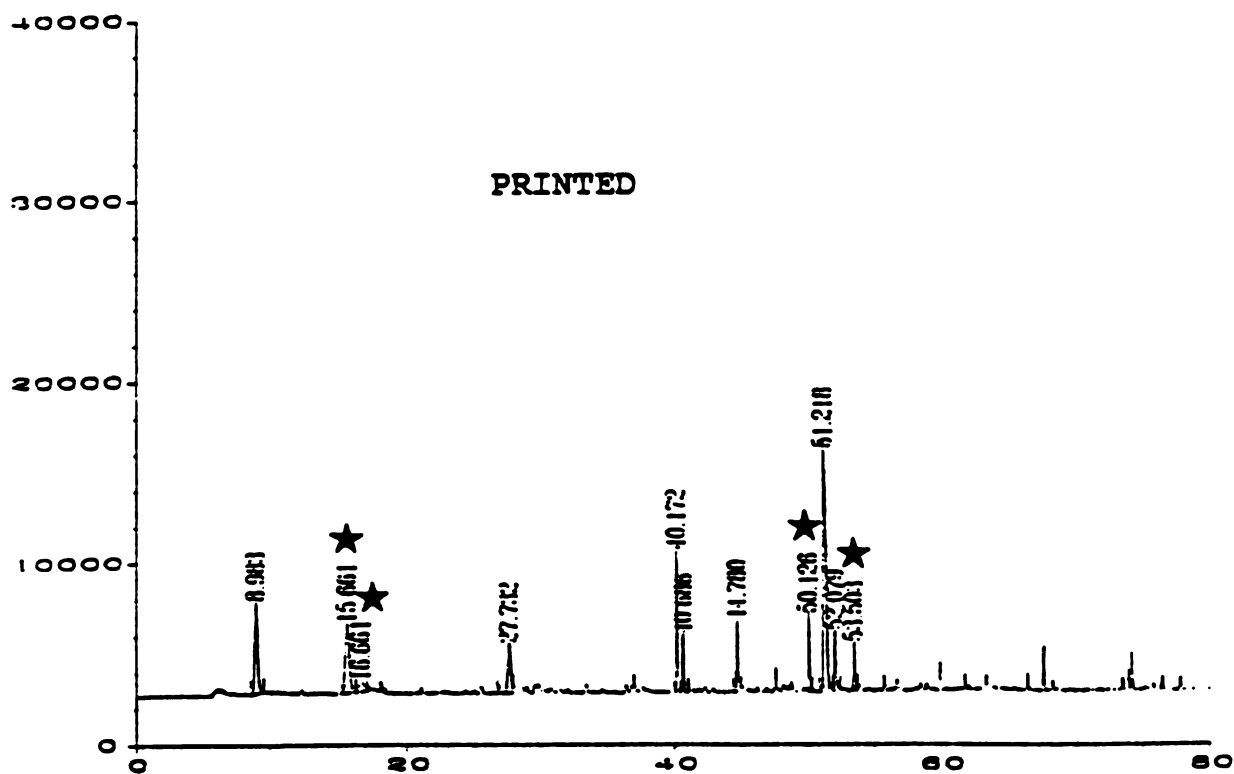
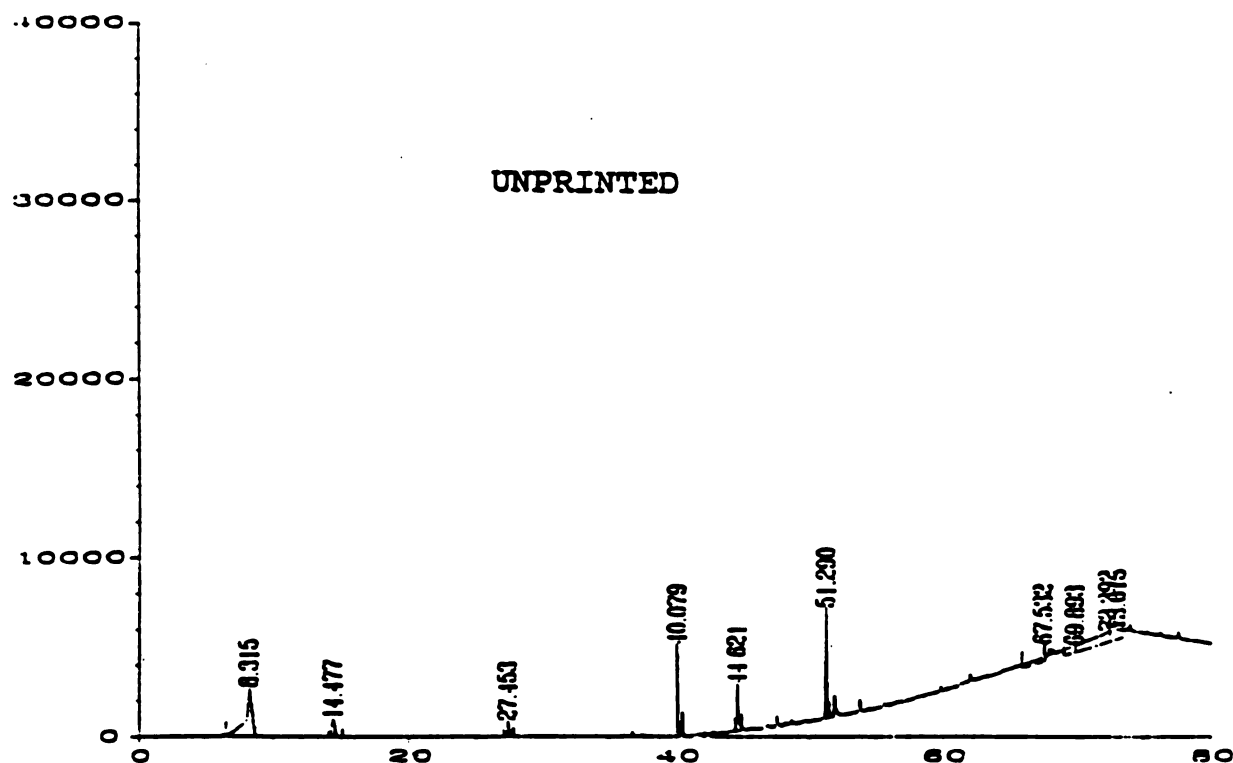


Figure 13. Chromatograms of volatile compounds found in water stored in unprinted and printed half-pint polyethylene coated, cartons from manufacturer "y".

★ = Peak present only in water stored in printed carton

### Solvent Extraction

The HPLC grade water (Fisher Scientific, Fair Lawn, NJ), stored in formed, printed cartons obtained from the three major manufacturers, was analyzed for the presence of off-flavor compounds. The cartons used for this analysis were from different lots than the cartons analyzed by thermal desorption procedure. Chromatograms obtained from the various samples are shown in Figure 14. Most of the peaks detected were found to be common in the treatment samples (x,y,z) and absent in the control sample (g). However, the intensity of the peaks varied among manufacturers, indicating differences in amounts of volatiles transferred from the package to the enclosed water. These results compare well with our sensory data and the thermal desorption studies.

The GCMS data were analyzed using the HP 5970 Chemstation Data System. The mass spectrograms obtained for each compound (peak) were compared to standard databases (EPA/NIH mass spectral data base, and NIST standard reference database series 1a). Eleven compounds were identified using this procedure. The group of compounds identified included, aliphatic hydrocarbons; aromatic hydrocarbons; phenol; and ester. These compounds along with their peak number, molecular weight and characteristic mass fragments are listed in Table 2. Samples from all the three manufacturers did not show the presence of all the identified compounds. 2,6-di-tert-

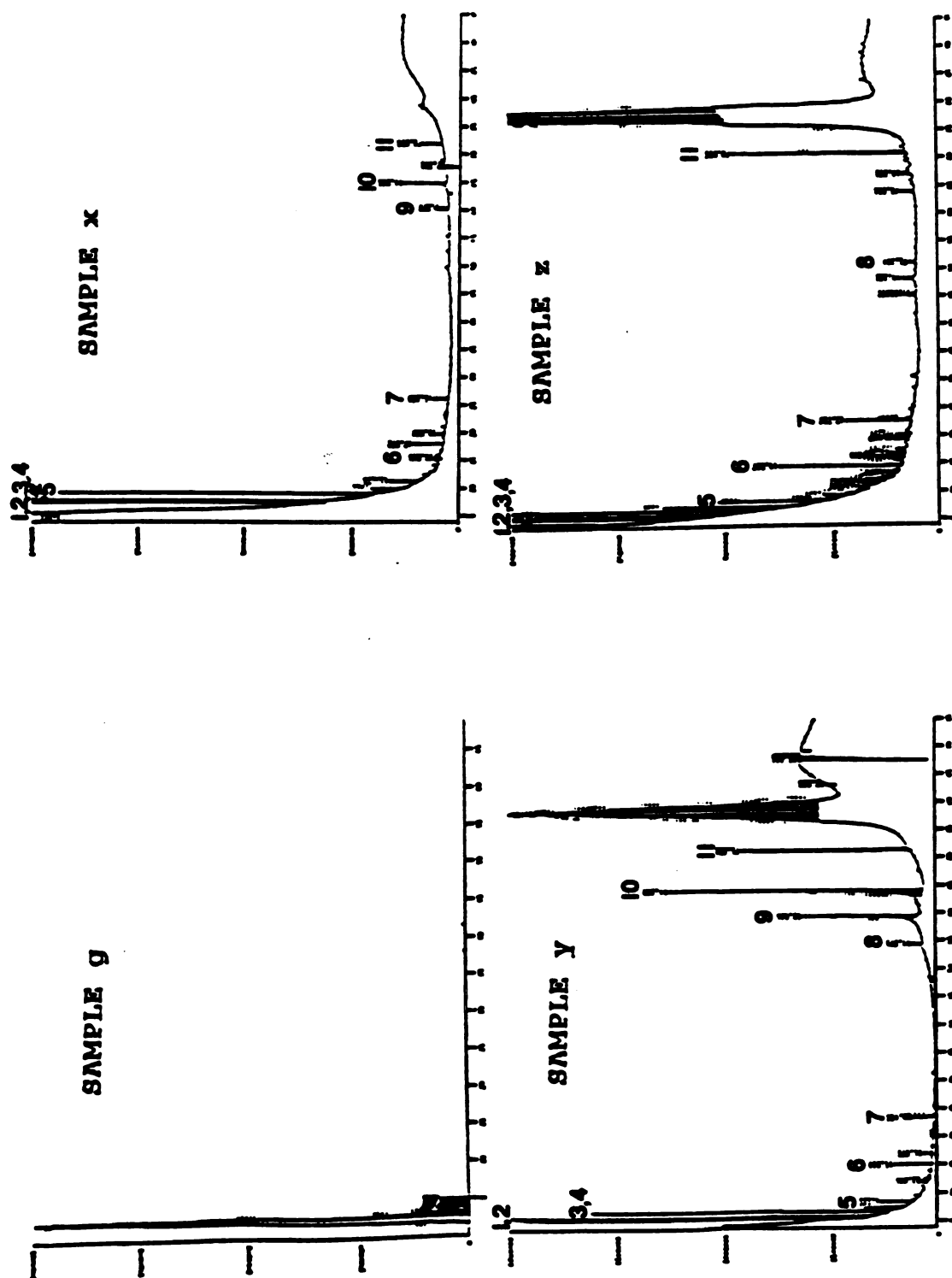


Figure 14. Chromatograms of volatile compounds found in water stored in unprinted half-pint polyethylene coated paperboard containers from the three (x, y & z) manufacturers and water stored in a glass container (g) using solvent extraction and GC-mass spectrometry.



Table 2. Characteristic Mass Fragments and their relative abundances of largest peaks

Peak <sup>a</sup> #	Compound	MW	Characteristic Mass Fragments (Relative Abundance, %)
1	Ethyl benzene	106	39 (10), 51 (13), 65 (9), 77 (8), 78 (8), 91 (100), 92 (8), 105 (6), 106 (32)
2	Benzene 1,4-dimethyl	106	39 (10), 51 (13), 63 (8), 65 (8), 77 (15), 78 (8), 79 (9), 91 (100), 105 (20), 106 (37)
3	Benzene 1,3-dimethyl	106	39 (18), 51 (15), 52 (8), 65 (8), 77 (14), 78 (8), 79 (8), 91 (100), 105 (29), 106 (65)
4	Benzene 1,2-dimethyl	106	39 (21), 51 (17), 65 (10), 77 (15), 78 (8), 79 (8), 91 (100), 105 (17), 106 (40)
5	Nonane	128	41 (40), 42 (16), 43 (100), 55 (13), 56 (17), 57 (67), 71 (20), 85 (24)
6	Decane	142	41 (40), 42 (14), 43 (100), 55 (14), 56 (17), 57 (90), 71 (33), 85 (24)
7	Undecane	156	41 (45), 42 (16), 43 (100), 55 (15), 56 (15), 57 (86), 71 (36), 85 (21)
8	Ionol (BHT)	220	41 (10), 55 (13), 57 (27), 67 (8), 81 (11), 145 (10), 205 (100), 206 (15), 220 (27)
9	Bicosane	282	41 (43), 43 (91), 55 (28), 56 (15), 57 (100), 69 (14), 70 (12), 71 (67), 85 (48)
10	Docosane	310	41 (43), 43 (79), 55 (32), 56 (18), 57 (100), 69 (17), 70 (13), 71 (74), 85 (57), 99 (19)
11	Di(2-ethylhexyl)phthalate	390	41 (9), 43 (21), 55 (10), 57 (32), 70 (18), 71 (21), 113 (10), 149 (100), 150 (11), 167 (29)

<sup>a</sup> Peak number for each compound is marked on the chromatograms shown in Figure 14.

butyl-p-cresol (BHT) was absent in sample "x" whereas, "z" showed the absence of eicosane and docosane.

Berg (1980) isolated similar groups of compounds from the PE-coated paperboards. The groups of compounds isolated were: saturated aliphatic hydrocarbons; unsaturated aliphatic hydrocarbons; aromatic hydrocarbons ; aromatic hydrocarbons with an unsaturated side chain; volatile ketones and esters.

Bojkow et al. (1977, 1979) identified the following compounds in fresh pasteurized milk packaged in PE coated cartons: unsaturated aliphatics, free fatty acids and compounds with alcoholic structures. They detected the presence of Platinol AH (di[-2-ethylhexyl]phthalate) and BHT (2,6-di-tert-butyl-p-cresol) in almost all the material tested. Our results correlate well with this study, as we were able to isolate similar compounds in almost all the packaging material tested.

The hydrocarbons were most likely contributed by the polyethylene coating. BHT is widely used as an antioxidant in food packaging. Di(2-ethylhexyl) phthalate might have accompanied the pigments or printing inks used on the packages (Bojkow et al., 1977). Di(2-ethylhexyl) phthalate is also a very commonly used plasticizer. It has been found to be the major precursor in formation of volatile compounds in PVC films and glassine packages (Kim and Gilbert, 1989; Kim et al., 1987). It has a characteristic undesirable odor which can contribute to the off-flavor in packaged food.

The origin of alkyl benzenes is unclear.

Standard curves were made for BHT, di(2-ethylhexyl) phthalate and Nonane (hydrocarbon occurring in highest quantity). Standard curves were constructed under same conditions for purge and trap, extraction, concentration and GCMS, as used for the unknown samples. The standard curves for the three compounds are shown in Figure 15 and the calibration data is presented in Appendix M. Nonane data was used to estimate the quantity of the other hydrocarbons and alkyl benzene compounds. The amount of these compounds present in cartons, varied within the same stock and among the manufacturers. The levels of these compounds detected in the water samples stored in half-pint cartons are shown in Table 3. Sample "x" showed the lowest concentration for all compounds, followed by "y" and "z". This might be because of the lower surface area exposed to the enclosed product in case of carton "x". Carton "x" had a surface area of 186.2 cm<sup>2</sup> (Table 1). Cartons "y" and "z" had a higher surface area of 198.93 cm<sup>2</sup>, thus allowing the transfer of higher amounts of volatiles into the enclosed product. Also, we see from Table 1 that carton "x" had the highest polyethylene film weight of 16 lbs./3,000 sq.ft., followed by cartons "y" and "z". Thicker coating of polyethylene in carton "x" might be responsible for the low concentration of the volatile compounds migrating from paperboard and printing ink to enclosed product.

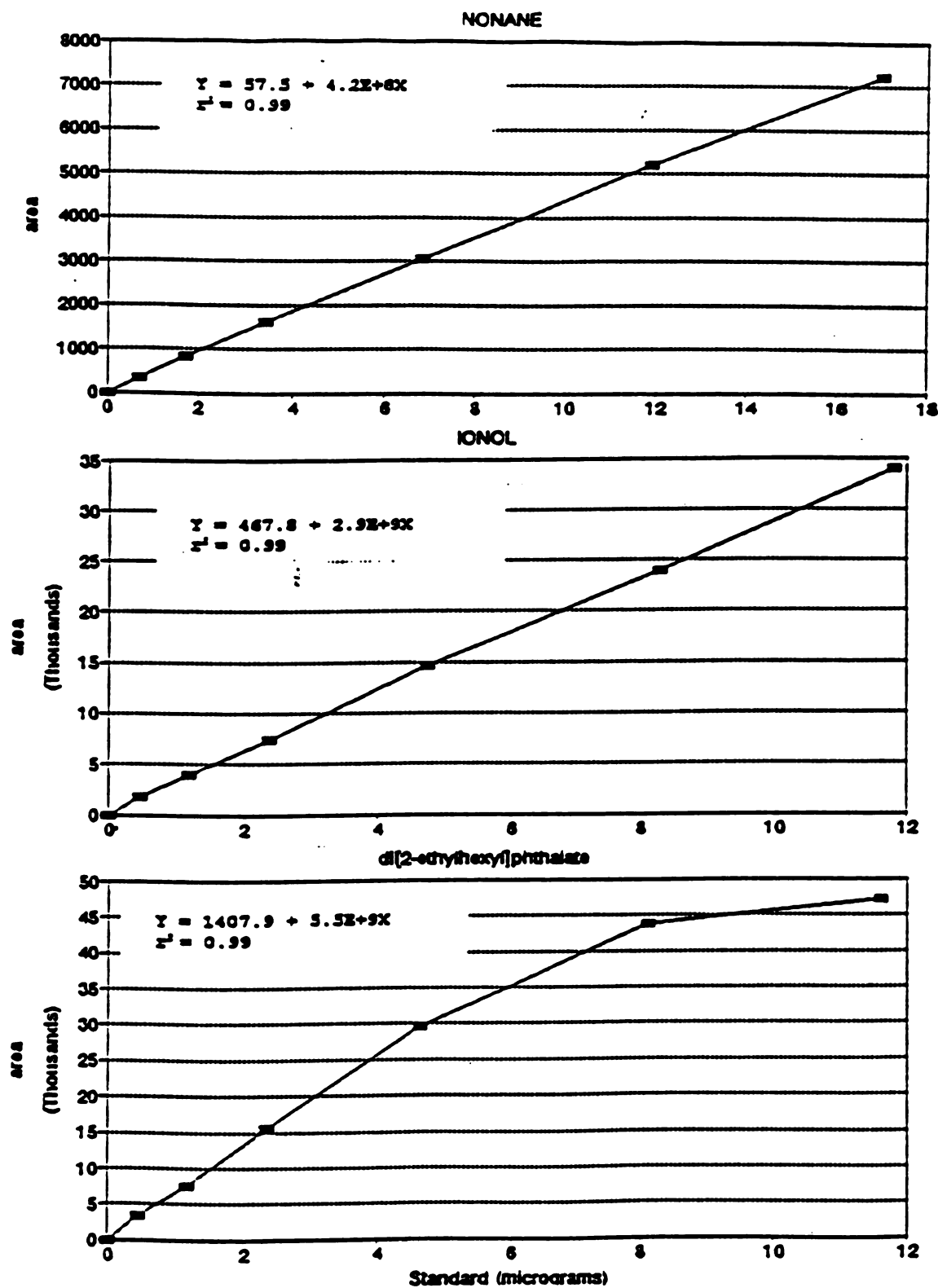


Figure 15. Calibration curves for nonane, ionol and di[2-ethylhexyl]phthalate constructed by running the known concentrations of standards under the conditions of purge & trap, solvent extraction and GCMS similar to unknown samples.



Table 3. Concentration of compounds responsible for "packaging flavor" in water enclosed in PE coated paperboard cartons from three manufacturers.

Compound	Sample x (mg/l) <sup>a,b</sup>	Sample y (mg/l) <sup>a,b</sup>	Sample z (mg/l) <sup>a,b</sup>
Ethylbenzene	0.6 (0.2)	12.1 (1.2)	14.3 (0.9)
Benzene 1,4 dimethyl	1.5 (0.3)	6.6 (0.3)	12.9 (0.6)
Benzene 1,3 dimethyl	0.7 (0.1)	3.2 (0.4)	46.7 (2.5)
Benzene 1,2 dimethyl	8.6 (0.2)	3.2 (0.1)	25.3 (2.0)
Nonane	8.4 (0.5)	27.3 (1.0)	65.0 (2.8)
Decane	0.5 (0.3)	7.5 (0.6)	9.7 (0.7)
Undecane	1.1 (0.2)	5.3 (0.4)	6.3 (0.3)
BHT	-	1.7 (0.5)	2.5 (0.4)
Eicosane	0.9 (0.2)	21.7 (2.8)	-
Docosane	3.4 (0.2)	39.0 (4.3)	-
Di(2-ethylhexyl) phthalate	6.4 (0.5)	21.2 (1.0)	27.4 (1.6)

<sup>a</sup> Mean of three samples

<sup>b</sup> Value in parenthesis is the standard deviation

The effectiveness of the analytical procedure was calculated in terms of percent recovery for the three compounds. The percent recovery data and calculations are shown in appendix N and O. The average recovery for each of the three compounds from Tenax and concentration technique was:

Nonane	89.5%
Ionol (BHT)	90.6%
Di(2-ethylhexyl)phthalate	77.5%

The average recovery for the three compounds from purge and trap, Tenax and concentration technique was:

Nonane	77.9%
Ionol (BHT)	78.2%
Di(2-ethylhexyl)phthalate	66.4%

The solvent extraction technique resulted in the detection of 66 to 78 percent of the amount of standard compound used. Twenty two to thirty four percent of the compound was lost during the sample preparation. Some compounds present in trace amounts in the original sample may get lost during the sample preparation using the solvent extraction technique.

A proposal to add these compounds to milk and use a trained panel to ascertain the compound(s) responsible for packaging flavor was submitted to University Committee on Research Involving Human Subjects (UCHRIS) at Michigan State University. Due to the absence of any established tolerance levels for safe human exposure to the chemicals, UCHRIS

review committee did not give approval to conduct this study. Therefore, the contribution of these compounds to packaging flavor in milk could not be studied at this time.

### **CONCLUSIONS**

The volatile compounds migrated from the milk carton to the enclosed product during storage. Eleven compounds were identified in water samples in contact with the formed milk cartons from the three major manufacturers. Cartons with the least surface area to volume ratio and thickest polyethylene coating (cartons "x") showed the least concentrations of these volatile compounds in the enclosed product. The degree of "packaging flavor" varied between different cartons from the same stock, and also between cartons obtained from different manufacturers. Amount and type of compounds migrating from different sections of the package was studied. It was found that heat sealing of cartons did not contribute excessive amounts or type of these compounds to enclosed product. All sections (side panel with and without heat seal, base or top) of milk cartons contributed equally to the packaging flavor.

## **SUMMARY AND CONCLUSIONS**

Fresh, pasteurized, homogenized, 2% fat milk, packaged in half-pint (236 ml) PE-coated paperboard containers and gallon (3780-ml) blow molded, high density polyethylene (HDPE) containers, was obtained from a local dairy processor immediately after processing and packaging. The HDPE-packaged milk was immediately transferred into clean 4000-ml Pyrex Erlenmeyer flasks. Half-pint cartons obtained from the three major carton manufacturers were filled with water and evaluated by an 11-member trained sensory panel using a paired comparison test. Milk and water stored in glass containers were used as controls. All samples of milk and water were stored for 3 d at 2.2 °C before being subjected to analysis. The water samples were also analyzed using purge and trap, solvent extraction and/or thermal desorption followed by gas chromatography and mass spectrometry.

Nine groups of school children took part in the evaluation of milk packaged in gable-top containers. Three groups showed a significant preference for milk stored in the glass container (control) versus the milk stored in the gable-top cartons. The rest of the groups had greater than fifty percent preferring the control milk but the results

were not significant at the  $p < 0.1$  level. The data was also analyzed for total number of elementary school children (grades 2nd through 5th). The combined data showed that elementary school children preferred the control versus the milk stored in the gable-top cartons. The results were found significant at  $p < 0.01$  level. The storage of milk for 3 days at  $2.2^{\circ}\text{C}$ , in polyethylene coated paperboard cartons imparted an off-flavor to the packaged milk. This off-flavor was responsible for children preferring milk stored in glass containers over milk stored in PE-coated paperboard cartons.

The results from the sensory studies by the trained panel suggested that the water samples stored in half-pint cartons from the three manufacturers had significantly more packaging flavor than samples stored in glass containers. The milk cartons from the three manufacturers contributed different levels of "packaging flavor", to the stored water, but they all showed significantly higher levels of "packaging flavor", than the water stored in a glass container.

The gas chromatographic and mass spectrometric analysis indicated the possibility of some volatiles from the paperboard, permeating the PE coating of the carton into the stored product. Comparison of chromatograms of water stored in a milk carton to the carton material indicated that volatiles were migrating from the packaging material into the water sample. The water stored in the cartons from the

three manufacturers showed peaks which were absent in the control, supporting the absence of packaging flavor in the control samples. All sections (side panel with and without heat seal, base or top) of milk cartons contributed equally to the packaging flavor.

Eleven compounds were identified using this technique. The groups of compounds identified included, aliphatic hydrocarbons; aromatic hydrocarbons; phenol; and ester. Their concentrations in water enclosed in half-pint milk carton were found to be in parts per billion range. Concentration of these compounds varied among different cartons from the same stock, and also among cartons obtained from different manufacturers. Cartons with the least surface area to volume ratio (cartons "x") showed the least concentrations of these volatile compounds in the enclosed product and also showed the least packaging flavor as detected by sensory panel.

Maintaining or increasing milk consumption has been and continues to be a major focus of the dairy industry. Children at school are major consumers of milk, and school milk is primarily packaged in PE-coated, gable-top paperboard containers. This study clearly demonstrated that "packaging flavor" developed in milk and water packaged in half-pint PE-coated cartons after three days of storage. The sensory studies with school children showed that children preferred the milk stored in the glass containers over the milk stored in PE-coated, paperboard containers.

Given these findings, the investigators would like to continue research in cooperation with packaging manufacturers in the following areas:

1. Our first step will be to study the relationship between quantity of compounds migrating from package components into milk stored in half-pint gable top, paperboard cartons and fat content of milk (Appendix P). Partitioning of off-flavor compounds between aqueous and lipid phase of the milk system will be studied by storing milk with different fat levels in gable-top cartons. After storage, the lipid part will be separated from aqueous phase and both parts will be tested for concentration of various compounds migrated from packaging. Partitioning coefficients will be calculated and models will be developed to predict the concentration of these compounds, partitioning into two phases of milk.
2. Other forms of milk and dairy product packaging will be surveyed for possible off-flavor development resulting from packaging component(s) migration. If the off-flavor is detected, methods will be developed to identify the compound(s) responsible for this defect.
3. Materials need to be developed for manufacture of gable top containers that will prevent migration of off-flavor compounds into the product (milk).

## APPENDICES



**APPENDIX A****Codesheet for Consumer Panel**

Date:

Type of samples: 2% fat milk after 3 days storage at 2.2 °C

Type of test: Acceptability (one sample per test) and  
paired preference test

Sample identificationCode

Half-pint gable-top paperboard container

E

Glass

G

Code serving containers as follows:

<u>Panelist</u>	<u>Order of</u>			<u>Panelist</u>	<u>Order of</u>		
<u>No.</u>	<u>Presentation</u>			<u>No.</u>	<u>Presentation</u>		
1	E	G	EG	2	GE	G	E
3	G	E	EG	4	GE	E	G
5	E	EG	G	6	G	GE	E
7	G	EG	E	8	E	GE	G
9	EG	E	G	10	G	E	GE
11	EG	G	E	12	E	G	GE
13	E	G	EG	14	GE	G	E
15	G	E	EG	16	GE	E	G
17	E	EG	G	18	G	GE	E
19	G	EG	E	20	E	GE	E
21	EG	E	G	22	G	E	GE
23	EG	G	E	24	E	G	GE
25	E	G	EG				

**APPENDIX B****Milk Taste Scoresheet For Consumer Panel**

Child's name \_\_\_\_\_

1. Please taste the milk samples \_\_\_\_\_ and \_\_\_\_\_, and  
circle the number you prefer.

\_\_\_\_\_

2. How old are you, as of your last birthday?

\_\_\_\_\_ years old.

3. Which grade are you in?

\_\_\_\_\_ grade.

4. Are you a:

Girl

Boy

A place to make any  
comments: \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

## APPENDIX C

## Milk Taste Scoresheet For Consumer Panel

Child's name \_\_\_\_\_

1. Please taste the milk sample \_\_\_\_\_, and circle the words that tell how much you like the sample.

Super	Really	Good	Just	Maybe	Just	Bad	Really	Super
good	good		a	good	a		bad	bad
			little	or	little			
			good	maybe	bad			
				bad				

2. Please taste the milk sample \_\_\_\_\_, and circle the words that tell how much you like the sample.

Super	Really	Good	Just	Maybe	Just	Bad	Really	Super
good	good		a	good	a		bad	bad
			little	or	little			
			good	maybe	bad			
				bad				

2. How old are you, as of your last birthday?

\_\_\_\_\_ years old.

3. Which grade are you in?

\_\_\_\_\_ grade.

4. Are you a:

Girl

Boy

A place to make any  
comments: \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

## APPENDIX D

## Codesheet for Trained Panel

Date:

Type of Samples: Double distilled water after 3 day storage  
at 2.2°C

Type of Test: Paired comparisons

<u>Sample identification</u>	<u>Code</u>
Glass	g
Half-pint gable-top carton from Manufacturer "x"	x
Half-pint gable-top carton from Manufacturer "y"	y
Half-pint gable-top carton from Manufacturer "z"	z

Code serving containers as follows:

<u>Panelist No.</u>	<u>Order of Presentation</u>					
1	gx	gy	gz	xy	xz	yz
2	xg	yg	zg	yx	zx	zy
3	gx	yg	gz	yx	zx	yz
4	xg	gy	zg	xy	xz	zy
5	zg	xz	yz	gx	yg	xy
6	gz	zx	zy	xg	gy	yx
7	yg	xy	xz	gz	yz	gx
8	gy	yx	zx	zg	zy	xg
9	zy	zx	zg	yg	yx	xg
10	yz	xz	gz	gy	xy	gx
11	zy	gz	xy	zx	gy	gx

## APPENDIX E

## Sensory Evaluation Sheet for Trained Panel

NAME \_\_\_\_\_ DATE \_\_\_\_\_

TYPE OF SAMPLE \_\_\_\_\_  
\_\_\_\_\_

## INSTRUCTIONS

Taste the samples on the tray from left to right. Two samples are identical; one is different. Select the odd/different sample.

If no difference is apparent, you must guess.

Sets of three samples	Odd Sample	Comments
_____		
_____		
_____		

If you wish to comment on the reasons for your choice or if you wish to make a comment on product characteristics, you may do so under

Comments

\_\_\_\_\_  
\_\_\_\_\_

## APPENDIX F

## Sensory Evaluation Sheet for Trained Panel

Taste panelist no. \_\_\_\_\_

## Sensory Evaluation sheet

**for**

2% Fat Milk

Name \_\_\_\_\_ Date \_\_\_\_\_

**Please taste the samples in the order listed below.**

Determine which of the samples has more "packaging flavor" and indicate by placing an X next to the code.

Sample	More "packaging flavor"	Comments
_____	_____	_____
_____	_____	_____
_____		
_____	_____	_____
_____	_____	_____
_____		
_____	_____	_____

## APPENDIX G

## Data for Paired Comparison and Acceptability Test

Table 4. Paired comparison and acceptability test of 2% fat milk packaged in glass containers (control) and half-pint polyethylene coated, paperboard cartons after three days of storage at 2.2 °C.

School/Grade	Total no. of Responses <sup>a</sup>	No. Preferring control milk	Difference of acceptability rating
A/1st to 6th	110	58	+0.34 <sup>b</sup>
B/7th to 12th	77	40	+0.16
C/4th	57	35 <sup>d</sup>	+0.70 <sup>c</sup>
D/4th	63	47 <sup>d</sup>	+0.56 <sup>c</sup>
E/2nd	33	18	+0.12
F/3rd	57	33	+0.12
G/3rd	54	37 <sup>d</sup>	+1.67 <sup>c</sup>
H/4th	42	21	+0.86 <sup>c</sup>
I/5th	57	32	+0.69 <sup>c</sup>
Overall 3rd	132	82 <sup>d</sup>	+0.92 <sup>c</sup>
Overall 4th	177	111 <sup>d</sup>	+0.65 <sup>c</sup>
Overall 5th	75	42	+0.59 <sup>c</sup>
Total 2nd-5th	432	260 <sup>d</sup>	+0.68 <sup>c</sup>
Grand Total	542	320 <sup>d</sup>	+0.56 <sup>c</sup>

<sup>a</sup> Total number of 3 replications

<sup>b</sup>  $\alpha = 0.1$ ; <sup>c</sup>  $\alpha = 0.05$ ; <sup>d</sup>  $\alpha = 0.01$

## APPENDIX H

## Statistical Analysis of Consumer Panel Data

Type of samples: 2% fat milk after 3 day storage at 2.2 °C

Type of sensory test: Paired preference

Test objective: To determine if milk packaged in glass container is preferred over milk packaged in PE-coated paperboard containers.

Type of statistical test: Two-side Paired Comparison Test  
(Table 9, Meilgaard *et al*, 1987a)

Analysis of results:

<u>Total</u>	<u>No. Preferring</u>	<u>No. of favorable responses</u>		
<u>Responses</u>	<u>control milk</u>	<u>required for significance at:</u>		
		<b>10%</b>	<b>5%</b>	<b>1%</b>
110	58	62	64	67
77	40	46	48	50
57	35	35	36	39
63	47	40	41	43
33	18	22	23	24
57	33	35	36	39
54	37	34	35	38
42	21	27	28	30
57	32	35	36	39
132	82	73	75	79
177	111	97	99	104
75	42	46	48	50
432	260	229	233	24
542	320	286	290	298



## APPENDIX I

## Statistical Analysis of Consumer Panel Data

Type of samples: 2% fat milk after 3 day storage at 2.2 °C

Type of sensory test: Acceptance (Nine point Hedonic Scale)

Test objective: To determine if milk packaged in glass container is statistically more acceptable than milk packaged in PE-coated paperboard containers.

Type of statistical test: Paired t-test

(Table 4, Meilgaard et al., 1987)

## Analysis of results:

Each member of the consumer panel evaluated both samples.

The null hypothesis tested was  $H_0: u_1 = u_2$  (no difference)

Consequently, the paired t-test was:

$$t = \frac{\bar{\delta} \sqrt{n}}{S_{\delta}}$$

where,  $\bar{\delta}$  = average of the differences between two samples

$S_{\delta}$  = sample standard deviation of the differences

$n$  = total number of responses

The null hypothesis was rejected if the value of  $t$ , exceeded the upper - critical value of the t-distribution with  $(n-1)$  degrees of freedom.

Continued on next page:----->

# Statistical Analysis of Consumer Panel Data (Cont.)

The results obtained for the above calculations were:

School/Grade	Total no. of Responses <sup>a</sup>	$S_b$	$\delta$	t
A/1st to 6th	110	2.639	+0.341 <sup>b</sup>	1.355
B/7th to 12th	77	1.808	+0.163	0.791
C/4th	57	3.128	+0.701 <sup>c</sup>	1.692
D/4th	63	2.652	+0.563 <sup>c</sup>	1.685
E/2nd	33	0.972	+0.124	0.733
F/3rd	57	1.252	+0.127	0.766
G/3rd	54	6.189	+1.670 <sup>c</sup>	1.983
H/4th	42	3.081	+0.861 <sup>c</sup>	1.811
I/5th	57	3.074	+0.693 <sup>c</sup>	1.702
Overall 3rd	132	5.581	+0.922 <sup>c</sup>	1.898
Overall 4th	177	4.788	+0.651 <sup>c</sup>	1.809
Overall 5th	75	2.869	+0.595 <sup>c</sup>	1.796
Total 2nd-5th	432	7.749	+0.683 <sup>c</sup>	1.832
Grand Total	542	6.813	+0.561 <sup>c</sup>	1.917

<sup>a</sup> Total number of 3 replications

<sup>b</sup>  $\alpha = 0.1$ ; <sup>c</sup>  $\alpha = 0.05$ ; <sup>d</sup>  $\alpha = 0.01$

## APPENDIX J

## Statistical Analysis of Trained Panel Data

Type of samples: Double distilled water after 3 day storage

Type of sensory test: Paired comparisons

Test objective: To compare the intensity of "packaging flavor" in double distilled water packaged in cartons obtained from X,Y, and Z manufacturers and double distilled water in a glass container (control)

Type of statistical test: Pairwise Ranking Test - Friedman Analysis

Analysis of results:

The table below shows the number of times (out of 66) each "row" sample was chosen as being more off-flavored than each "column" sample.

		Column samples (less packaging-flavor)			
		g	x	y	z
Row samples	g	-	19	12	12
(more	x	47	-	18	24
packaging-flavor)	y	54	48	-	28
	z	54	42	38	-

where, g is water samples stored in glass container and x,y & z are the water samples stored in the cartons obtained from three manufacturers.

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### Statistical Analysis of Trained Panel Data (cont.)

To compute the rank for each sample, the rank sum of one is assigned to the more off-flavored and the rank of two to the less off-flavored sample. The rank sums are then obtained by adding the sum of the row frequencies to twice the sum of the column frequencies, e.g., for sample g,  $(12 + 19 + 12) + 2(54 + 47 + 54) = 353$

Sample	g	x	y	z
Rank sum	353	307	266	262

The test statistic, Friedman's T, is computed as follows:

$$\begin{aligned}
 T &= (4/pt) R^2 - (9p[t-1]^2) \\
 &= [4/(66)(4)] [353^2 + 307^2 + 266^2 + 262^2] - [9(66)(3^2)] \\
 &= 41.65
 \end{aligned}$$

where p = the number of times the basic design is repeated

t = the number of treatments

$R_i$  = the rank sum for the i'th treatment

$R^2$  = sum of all R's squared, from  $R_1$  to  $R_t$

The value of T is compared to the critical value of  $\chi^2$  with (t-1) degrees of freedom. The critical Ts are:

Level of significance, $\alpha$	0.10	0.05	0.01
Critical T	6.25	7.81	11.3

Here as we see that the value of  $T = 41.65$  is greater than all the critical values of T shown in above table, so we can say that a significant difference exists among the four samples.

The HSD (honestly significant difference) value for comparing two rank sums ( $\alpha = 0.05$ ) is:

$$\begin{aligned}
 \text{HSD} &= q_{\alpha, t, pt/4} \\
 &= 3.63 \quad (66)(4)/(4) = 29.49
 \end{aligned}$$

**APPENDIX K****Calculations for Contact Surface Area of Half-pint  
PE-coated Paperboard Cartons****Manufacturer X**

Contact surface area,  $A_{cx}$ , is

$$A_{cx} = A_1 + A_b$$

where  $A_1$  = lateral area  
 = area of four rectangles  
 =  $4 \times bh$   
 =  $4 \times (7.0)(4.9)$   
 =  $137.20 \text{ cm}^2$

$A_b$  = area of the base  
 =  $b^2$   
 =  $(7.0)^2$   
 =  $49.00 \text{ cm}^2$

$A_{cx}$  =  $137.20 + 49.00$   
 =  $186.20 \text{ cm}^2$

**Manufacturer Y and Z**

Contact surface area,  $A_{cx}$ , is

$$A_{cy} = A_1 + A_b$$

where  $A_1$  = lateral area  
 = area of four rectangles  
 =  $4 \times bh$   
 =  $4 \times (5.7)(7.3)$   
 =  $166.44 \text{ cm}^2$

$A_b$  = area of the base  
 =  $b^2$   
 =  $(5.7)^2$   
 =  $32.49 \text{ cm}^2$

$A_{cx}$  =  $166.44 + 32.49$   
 =  $198.93 \text{ cm}^2$

## APPENDIX L

## Calculations for Calibration Curve Development

IONOL

0.01 grams of ionol was added to 100 ml of HPLC grade water in a 100 ml volumetric flask providing an initial standard stock solution with a ionol concentration of 100 parts per million (ppm).

1. 0.25 ml of 100 ppm solution was added to 500 ml HPLC grade water in a 500 ml volumetric flask providing a solution with a ionol concentration of 50 parts per billion (ppb).
2. 100 ml of 50 ppb solution was added to 150 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 20 ppb.
3. 50 ml of 50 ppb solution was added to 200 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 10 ppb.
4. 25 ml of 50 ppb solution was added to 225 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 5 ppb.
5. 10 ml of 50 ppb solution was added to 240 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 2 ppb.

DI[-2-ETHYL-HEXYL]PHTHALATE

5 microliter of di[-2-ethyl-hexyl]phthalate was added to 50 ml of HPLC grade water in a 50 ml volumetric flask providing an initial standard stock solution with a di[-2-ethyl-hexyl]phthalate concentration of 98.1 ppm.

$$(0.981 \text{ g/ml})(0.005 \text{ ml}/50 \text{ ml})(1\text{E}+06) = 98.1 \text{ ppm}$$

1. 0.25 ml of 98.1 ppm solution was added to 500 ml HPLC grade water in a 500 ml volumetric flask providing a solution with a di[-2-ethyl-hexyl]phthalate concentration of 49.05 ppb.
2. 100 ml of 49.05 ppb solution was added to 150 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 19.62 ppb.
3. 50 ml of 49.05 ppb solution was added to 200 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 9.81 ppb.
4. 25 ml of 49.05 ppb solution was added to 225 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 5 ppb.
5. 10 ml of 49.05 ppb solution was added to 240 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 1.962 ppb.

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## Calculations for Calibration Curve Development(cont.)

NONANE

10 microliter of nonane was added to 50 ml of HPLC grade water in a 50 ml volumetric flask providing an initial standard stock solution with a nonane concentration of 144 ppm.

$$(0.72 \text{ g/ml})(0.01 \text{ ml}/50 \text{ ml})(1\text{E}+06) = 144 \text{ ppm}$$

1. 0.25 ml of 144 ppm solution was added to 500 ml HPLC grade water in a 500 ml volumetric flask providing a solution with a nonane concentration of 72 ppb.
2. 100 ml of 72 ppb solution was added to 150 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 28.8 ppb.
3. 50 ml of 72 ppb solution was added to 200 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 14.4 ppb.
4. 25 ml of 72 ppb solution was added to 225 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 7.2 ppb.
5. 10 ml of 72 ppb solution was added to 240 ml of HPLC grade water in a 250 ml volumetric flask for a concentration of 2.88 ppb.

**APPENDIX M**

**Data for Calibration Curve Development**



Table 5. Ionol Data for the Calibration Curve.

<u>Sample</u>	<u>Grams of Ionol in</u> <u>half-pint standard solution</u>	<u>Area Response</u>
1a	0.00	0
1b	0.00	0
Average		0
2a	4.72E-07	1801
2b	4.72E-07	1752
Average		1777
3a	1.18E-06	3836
3b	1.18E-06	3942
Average		3889
4a	2.36E-06	7213
4b	2.36E-06	7483
Average		7348
5a	4.72E-06	14254
5b	4.72E-06	14992
Average		14623
6a	8.26E-06	22970
6b	8.26E-06	24862
Average		23916
7a	1.18E-05	33506
7b	1.18E-05	34498
Average		34002

Table 6. Nonane Data for the Calibration Curve.

<u>Sample</u>	<u>Grams of Nonane in</u> <u>half-pint standard solution</u>	<u>Area Response</u>
1a	0.00	0
1b	0.00	0
Average		0
2a	6.80E-07	337
2b	6.80E-07	317
Average		327
3a	1.70E-06	826
3b	1.70E-06	811
Average		818
4a	3.40E-06	1635
4b	3.40E-06	1589
Average		1612
5a	6.80E-06	2731
5b	6.80E-06	2899
Average		2815
6a	1.19E-05	5004
6b	1.19E-05	5380
Average		5192
7a	1.70E-05	7198
7b	1.70E-05	7266
Average		7232

Table 7. Phthalate Data for the Calibration Curve.

<u>Sample</u>	<u>Grams of Pthalate in</u> <u>half-pint standard solution</u>	<u>Area Response</u>
1a	0.00	0
1b	0.00	0
Average		0
2a	4.63E-07	3346
2b	4.63E-07	3289
Average		3318
3a	1.16E-06	7470
3b	1.16E-06	7551
Average		7511
4a	2.32E-06	15233
4b	2.32E-06	15734
Average		15484
5a	4.63E-06	29157
5b	4.63E-06	30091
Average		29624
6a	8.10E-06	42917
6b	8.10E-06	44669
Average		43793
7a	1.16E-05	47598
7b	1.16E-05	46809
Average		47204

**APPENDIX N**

**Percent Recovery Data for Tenax and Concentration Technique**

Table 8. Percent Recovery Data for Nonane for tenax and concentration technique.

Solution 1 (40ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
1a	36926	32661
1b	33063	31367
Average	34995	32014
Recovery		91.5%

Solution 2 (100ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
2a	107029	89263
2b	111968	102192
Average	109499	95728
Recovery		87.4%

Average Recovery for Nonane: 89.5%

Table 9. Percent Recovery Data for Ionol for tenax and concentration technique.

Solution 1 (40ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
1a	72883	64199
1b	75973	71593
Average	74428	67896
Recovery		91.2%

Solution 2 (100ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
2a	174808	151713
2b	174133	162245
Average	174471	156979
Recovery		90.0%

Average Recovery for Ionol: 90.6%

Table 10. Percent Recovery Data for di[-2-ethyl-hexyl]  
phthalate for tenax and concentration technique.

Solution 1 (40ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
1a	57355	45655
1b	56330	42679
Average	56843	44167
Recovery		77.7%

Solution 2 (100ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
2a	81189	66964
2b	96539	70389
Average	88864	68677
Recovery		77.3%

Average Recovery for di[-2-ethyl-hexyl]phthalate: 77.5%

**APPENDIX O**

**Percent Recovery from Purge & Trap, Tenax  
and Concentration Technique**



Table 11. Percent Recovery Data for di[2-ethyl-hexyl]phthalate  
from purge & trap, tenax and concentration technique.

Solution 1 (40ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
1a	21423	13877
1b	21726	14095
Average	21575	13986
Recovery		64.8%

Solution 2 (100ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
2a	39533	27074
2b	40162	27113
Average	39848	27094
Recovery		68.0%

Average Recovery for di[-2-ethyl-hexyl]phthalate: 66.4%

Table 12. Percent Recovery Data for Nonane from purge & trap, tenax and concentration technique.

Solution 1 (40ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
1a	2065	1583
1b	2162	1684
Average	2114	1634
Recovery		77.3%

Solution 2 (100ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
2a	6886	5376
2b	6708	5297
Average	6797	5337
Recovery		78.5%

Average Recovery for Nonane: 77.9%

Table 13. Percent Recovery Data for Ionol from purge & trap, tenax and concentration technique.

Solution 1 (40ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
1a	24491	19403
1b	24502	19928
Average	24497	19666
Recovery		80.3%

Solution 2 (100ppm):

	Solution for	
	Basis	Extract
<u>Sample</u>	<u>Area Response</u>	<u>Area Response</u>
2a	30415	23037
2b	29881	22758
Average	30148	22898
Recovery		76.0%

Average Recovery for Nonane: 78.2%

**APPENDIX P****Proposal for Continued Research**

H<sub>0</sub>: The quantity of compounds migrating from package components into milk stored in half-pint gable top, paperboard cartons is directly related to the fat content of the milk.

Description of Procedure

This study will be done to study relationship of fat content of milk with migration of compounds from the packaging. Three types of samples will be analyzed to develop regression models, which can then be used to estimate the quantity of migrating compounds based on the fat % of milk. HPLC grade water, skim-milk, 2% fat and whole milk will be used as four sample treatments. Preformed half-pint cartons will be obtained from a local dairy processor. Cartons will be obtained on three different days to provide us with three replications. Three types of milk will be obtained in gallon jugs from the same dairy processor immediately after processing. Water and milk samples (236 ml) will be transferred into preformed half-pint milk cartons by using a syringe with a luer-lok tip inserted directly into the middle of the carton and stored for 3 days at 36°F. Samples will be stored in five cartons for each treatment in each replicate, and after storage, samples from 5 cartons will be mixed in a glass container. Two half-pint (236 ml) samples will be withdrawn and analyzed by solvent extraction and gas chromatography.

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**Proposal for Continued Research (cont.)**

Volatiles from the stored samples will be collected in tenax traps using purge and trap apparatus. Tenax traps will be packed and conditioned for 36 hours under nitrogen flow of 25 ml/min at 200 °C before being used for sample collection. Samples will be transferred to purge and trap apparatus and purged under 25 ml/min nitrogen flow for 24 hours. Volatiles will be extracted using 2 ml of hexane in the direction opposite to what was used for trapping. Hexane extracts will be concentrated to 0.5 ml using nitrogen sparging and transferred to amber colored crimp and seal glass vials. One microliter of the extract will be injected for gas chromatographic analysis. A total of twenty four samples will be run for this study.

2,6-di-tert-butyl-p-cresol (BHT) an antioxidant; di(2-ethylhexyl)phthalate (plasticizer) and nonane (hydrocarbon found in highest concentration) will be monitored during this study. Concentration of these compounds will be calculated in each sample using a standard curve for each compound. For preparation of standard curves, solutions will be made in hexane of known concentration for each standard and 1 ul will be injected into the GC. Four different concentrations will be chosen for each standard to provide us with a standard curve. A total of twelve samples will be run for this purpose. Regression equations will be developed for each standard and used to calculate the amounts of that compound in unknown samples. The actual concentration of these compounds isolated from half-pint (236 ml) samples will then be calculated from these values.

Continued on next page---->

**Proposal for Continued Research (cont.)**

Results for three replicates for each treatment will be averaged to get the mean value and standard deviations calculated. Data will then be subjected to regression analysis, and a regression model will be developed.

$$Y = A + BX$$

where, Y = Concentration of volatile

X = Fat % of milk

A = Intercept

B = Slope

Three separate regression models will be developed for the three compounds. These models can then be used to estimate the quantity of these compounds migrating from package into enclosed milk based on its fat content.

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## BIBLIOGRAPHY

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