MEASUREMENT OF VOLATILES FROM A SUSCEPTOR MATERIAL USING A THERMAL DESORPTION METHOD

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A THESIS

submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1991

ABSTRACT

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A thermal desorption method was developed and compared with the diffusion trapping and headspace techniques for measuring release of volatiles from a susceptor material. Samples of susceptor were cut into a specific size and sealed in a glass vial. In the headspace technique, the sample was heated in the microwave oven from 1 to 5 minutes and in an oil bath at 180, 200 and 220°C for periods ranging from 1 to 5 minutes. For diffusion trapping analysis, the sample was heated in an oil bath from 1 to 5 minutes at 180, 200 and 220°C, and the volatiles were trapped onto Tenax. The thermal desorption method was performed on samples heated in the thermal stripper at 180 and 190°C for purging times of 1 to 5 minutes. The susceptor volatiles were absorbed by Carbotrap 300 and the volatiles were desorbed in the thermal desorption unit. Six compounds, 2-methyl-propanol, n-butanol, styrene, 2-butoxyethanol, furfural and 2-(2-butoxyethoxy)ethanol, were detected and quantified by gas chromatography. At a temperature of 180°C, the thermal desorption method was much more sensitive than the headspace technique and diffusion trapping method.

To I-Feng, Hsien-Chih and my parents for their support.

ACKNOWLEDGEMENTS

The author expresses sincere appreciation to Dr. Bruce Harte for his guidance and encouragement during this study.

Sincere appreciation is extended to the guidance committee: Dr. Jack Giacin and Dr. Ian. Gray for their assistance and advice. Special thanks are expressed to Dr. Parvin Hoojjat for sharing her time and expertise in method development and interpretation of the results.

I would also like to thank my friends Chin-Gin Low, Chia-Hung Lin, Kuo-Chung Yin, Shuh-Hsin Chou and Chit Leong for their assistance in typing and editing this document.

Finally, I would like to express my deepest thanks to my boy friend I-Feng, my brother Hsien-Chih and my parents for their love, encouragement and support throughout this graduate study.

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CHAPTER 1

INTRODUCTION

The food industry has developed a whole new generation of products which appeal to the 85% of consumers that use microwave ovens (Huang, 1987). These products can be "cooked in the package", which makes them convenient to prepare and use. Microwave "in package" heating can be used in several applications including: defrosting, cooking/reconstitution, baking, frying and pasteurization/sterilization. For defrosting, the product/package material temperature will generally not exceed 100°C. In cooking and reconstitution, the temperature of the product/package will depend upon product moisture content, sugar, protein and fat content, product morphology and packaging material. Temperatures above 100°C may result as moisture evaporates in localized areas. If product crisping and browning are desired, product temperature can exceed 200°C.

There are essentially four different package types designed for microwave "cooking in the package". These include transparent materials, absorbing (susceptor) materials, shielding and field modification. Of these, transparent and susceptors predominate. The transparent materials allow direct microwave radiation through the

package and into the food, therefore, package heating occurs through contact with a hot product.

Absorbing materials (susceptor) are used where product crisping, browning or other-heat induced reactions are desired. The most common microwave susceptor material currently in use is metallized (aluminum) polyethylene terephthalate (PET) laminated to paperboard or paper. The metallized PET film absorbs microwave energy by coupling with the electrical field component of the microwave radiation to cause heating. During normal use, these packages have been shown to heat to 250°C (Lentz and Crossett, 1988). The National Food Processors Association (Kashtock et al., 1990) measured the interface temperature of commercial brands of popcorn and pizza cooked on susceptors. The popcorn packaging material interface temperature reached 207°C (404°F), which the pizza package interface was 190°C (375°F).

Since the PET susceptor can achieve elevated temperatures which are much higher than the glass transition temperature of PET (Tg=80°C) there is a greater potential for thermal damage to the susceptor package and increased migration of package components to foods. Hollifield (1988) demonstrated that: (1) at the temperature achieved during microwave heating (>500°F), susceptor packaging components begin to break down, (2) there does not appear to be a functional barrier between the food and adhesive/paperboard

layers and that, (3) significant migration of polyester oligomers occur into corn oil. If the migrants are absorbed by food products, they may affect the safety and quality of the food.

The Food and Drug Administration (FDA) has expressed concern about these materials because there is no current regulation which covers their use at such extreme temperatures. Consumer advocates also question the safety of susceptors in microwave heating. Articles in publications such as the Wall Street Journal (Nazarrio, 1990), New York Times and The National Examiner (Anon, 1990) have focused attention on susceptors.

Two analytical procedures are being used for the analysis of trace volatiles from susceptor packaging; these include static headspace (ASTM, 1990) and diffusion trapping methods. These techniques allow only a relatively small volume of sample to be injected through a syringe or gas sampling loop onto a GC column or sorbet trap. Reproducibility of these analyses are dependent on all sampling parameters being held absolutely constant. Slight deviations in temperature, pressure, sample matrix or volume may cause drastic changes in the volatile composition. Both techniques also require extensive labor and substantial analysis time.

The purpose of this study was to develop and compare test methodologies used to quantify levels of volatile

compounds which may migrate from susceptor packaging material during heating.

In the method developed volatile compounds from the susceptor are absorbed onto a solid support in a closed chamber. The volatiles are then thermally desorped and swept with carrier gas into a GC. The gas passes through the sorbet material continually until all of the trace components are collected, thereby increasing the concentration level over that of static headspace and diffusion trapping methods.

The specific objectives of the project are:

1. To develop a thermal desorption method to measure the volatiles released from a susceptor material during heating.
2. To compare the sensitivity of the headspace method, diffusion trapping technique and thermal desorption procedure at 180°C.
3. To determine the effect of various heating times on the release of volatile migrants from the susceptor at different heating temperature.

CHAPTER 2

LITERATURE REVIEW

2.1 Microwave Package Market and Development

The home microwave market is expected to grow from 73% in 1988 to 94% by 1993 (Schotland Business Research, 1990). Food packaged for the microwave market had a retail value of $5 billion in 1988, and will grow to $7 billion by 1993.

In the marketing of microwave food, there are four major categories: frozen meals, refrigerated meals, dry packaged meals and moist, shelf-stable foods. The market for frozen entrees have matured (Table 1). Product quality is a competitive weapon in which to gain retail shelf space. Refrigerated offerings of entrees and side dishes will proliferate as well as moist, shelf-stable products. Non-frozen products provide the ultimate in convenience since they can be heated in a microwave in 20%-30% of the time required for their counterparts. In addition, non-frozen products heat more uniformly, thereby reducing the problem of hot and cold spots. From an economic standpoint, distributing shelf stable foods are 25% of the cost of distributing frozen foods because of difference in transportation cost, warehouse freezer cost, etc. (Rothenberger, 1987)

Table 1. U.S. retail microwavable food market[b]

	1990	1992	1994
Frozen meals	2159[a]	2348	2544
Refrigerated meals	120	310	488
Dry packaged meals	131	380	552
Moist, Shelf-Stable	438	804	1173

a. units : in millions

b. source : Packaging Strategies, 1989

To be effective in the microwave market, the packaging industry needs to address the migration problems inherent in microwave package preparation of foods. To design high quality microwave food, one must first understand the heating behavior of food in the microwave oven, and how packaging materials influence and are affected by the microwave environment.

2.2 Microwave Properties

Microwaves are electromagnetic waves, which are located between radio and infra-red regions in the electromagnetic spectra (Figure 1). Electromagnetic waves have a characteristic wavelength (λ) and frequency (f), and there is an inverse relationship between them (equation 1),

$$\lambda = \frac{C}{f} \qquad (1)$$

where C is the speed of light (3×10^{10} cm/sec), λ is the wavelength (cm) which is the length of one cycle and f is frequency (Hz) which is the number of cycles per second (Knutson, et.al., 1987). Microwave frequencies of 915, 2450, 5800 and 22125 MHz are used for industrial, scientific and medical microwave ovens, with 2450 MHz being the most used in home microwave ovens (Copson, 1975).

Like all electromagnetic energy , microwaves exhibit both electric (E) and magnetic fields (H) (Figure 2). The electric field is oriented in the Y-direction, and the

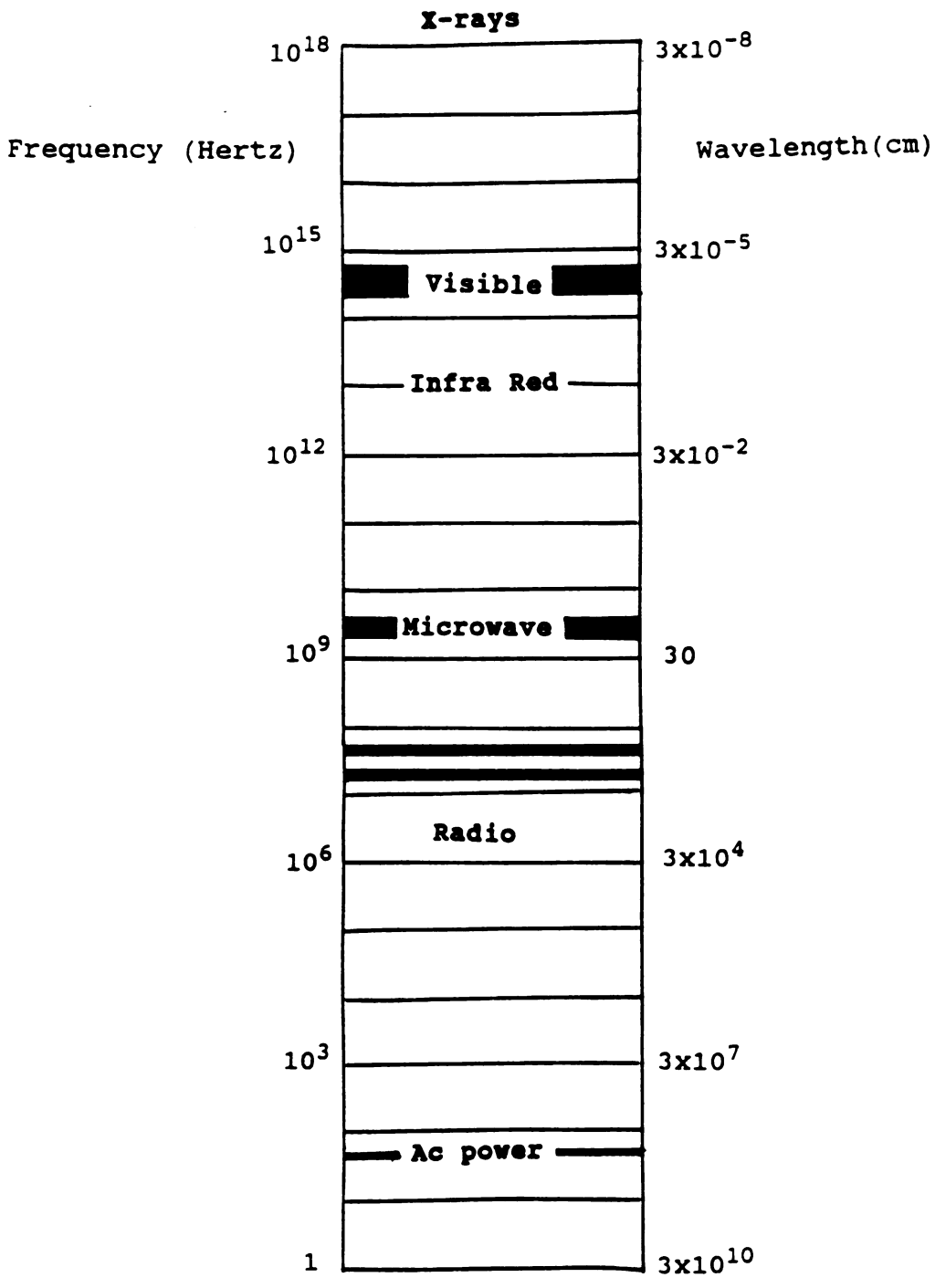

Figure 1. The electromagnetic spectrum. (Hasiam, et.al, 1972)

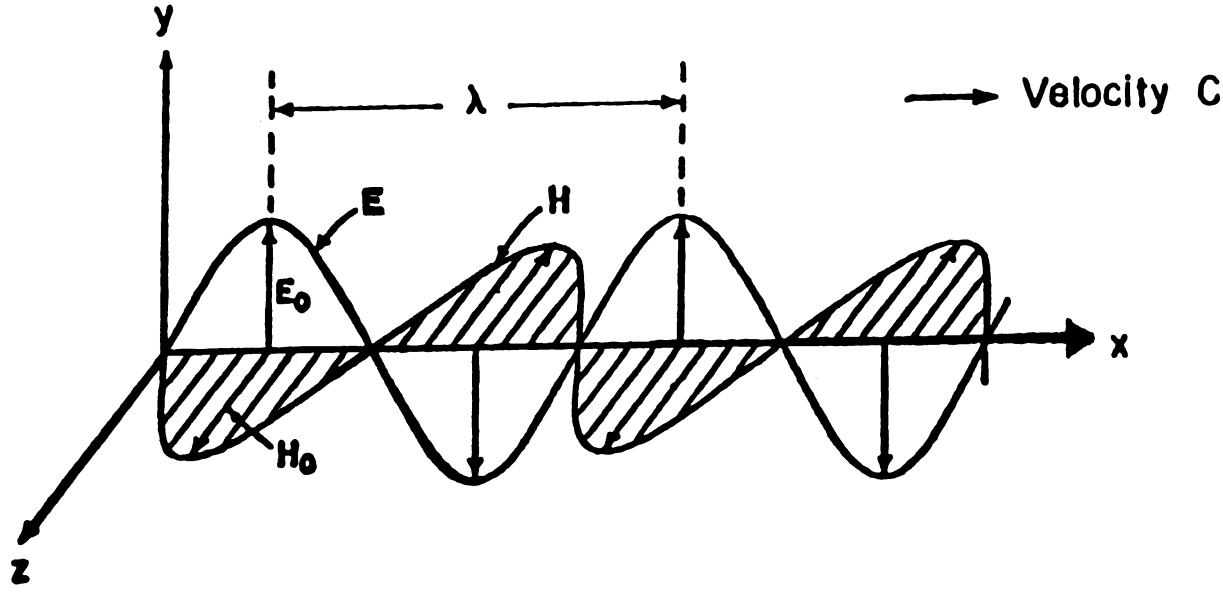

Figure 2. A plane monochromatic electromagnetic wave.
(Rosenkranz and Higgins, 1987)

magnetic field is oriented perpendicular to the electric field (Rosenkranz, 1987). Materials that have molecular dipoles or mobile electrons are affected by these fields. The dipoles and ions realign themselves to the rapidly changing electrical field. The molecular motion causes product heating in the microwave oven.

2.3 Microwave Heating Generation

Microwave heating is fundamentally different from traditional conventional cooking, as shown in Table 2 (Bohrer, 1987). In conventional heating, thermal energy is transferred from product surfaces toward their center 10-20 times more slowly than in microwave heating. In contrast, microwave heating is caused by wave penetration into the food. The interaction of the chemical constituents of foods with the electromagnetic field induces heating.

During microwaving, the magnetic field component of the microwave radiation interacts with ferrous metals. However, another major factor which results in generation of heat within a product is the electric field interaction. The electric field component of microwave radiation interacts with dielectric materials (ex. water molecules) in the food. Water molecules are rotated by forces of attraction and repulsion from oppositely charged regions of the electric field. This causes disruption of hydrogen bonds between H_2O molecules and generates heat by "molecular

Table 2. Comparison between conventional and microwave ovens

Conventional Oven	Microwave Oven
. Hot air convection	. Polar molecule excitation
. Air hotter than food	. Air cooler than food
. Heat conducted from surface	. M/W's penetrate food
. Conduction differences relatively small	. Absorption differences relatively large
. Surface dehydration before interior	. Surface and interior dehydrate
. Surface browning before bulk dehydration	. Surface browning after bulk dehydration

Source : Bohrer, 1987

friction " (Mudgett,1989). The heat is transferred through the whole product by conventional thermal conduction.

Molecular friction results primarily from the disruption of weak hydrogen bonds associated with the dipole rotation of free water molecules and with the ionic conduction of free salts in an electrical field of rapidly changing polarity (Decareau, 1986).

Dipole rotation is dependent on the microwave frequency and product temperature (White,1975). Due to the nonspherical shape of dipolar molecules, rotation is limited and orientation is randomized. When the wave magnitude of an electrical field goes up during microwave heating, the molecular orientation becomes ordered. As the electrical field goes down, ordered molecules become random once more. Through this process, there is conversion of energy from electric field energy to stored potential energy, and then to random kinetic or thermal heat in the material (White,1975).

Ionic conduction is caused when polar molecules break apart to form positive and negative ions. These ions are electrically charged and align with the electric field. This creates a current flow which is essentially kinetic energy. When these ions collide with other molecules, the kinetic energy is converted into heat. These molecules may collide a thousand times during their exposure to microwaves. The electrical field may be either continuous

or intermittent, ionic conduction will occur in either case. Therefore, ionic conduction can be accelerately in the presence of an electrical field and energized upon impacting with other ions.

2.4 Factors Affecting Microwave heating

Product heating rate in a microwave is influenced by penetration depth and conventional heat transfer, which are affected by the electrical and physical properties of food (Mudgett,1989).

2.4.1 Electrical Characteristic

Two values are used to characterize electrical properties of food; the relative dielectric constant (k′) and the loss factor (k″). The dielectric constant is a measurement of a material's ability to store electrical energy. The loss factor reflects its ability to dissipate electrical energy as heat. The ratio of loss factor (k″) to dielectric constant (k′) is defined as the loss tangent:

$$\tan\theta = \frac{k''}{k'} \qquad (2)$$

Both the loss factor and loss tangent are defined as the "lossiness" of a material, and are used to describe the energy which is absorbed and convert to radiant heat. The larger a material's losseness, the more power it will absorb. Increased power absorption will cause a higher temperature increase within a material (Perry, 1987).

The dielectric constant determines the speed of the electromagnetic waves as they travel through a food. The larger the dielectric constant, the slower the velocity of the microwaves. This effect is more pronounced at the interface between food and air. If the dielectric constant is larger than that of air (dielectric constant of air is 0), the microwave will be reflected off the surface of the food. Therefore, most foods do not brown or crisp in the microwave oven (Mudgett, 1986). Some polar compounds, like sugar, will change the dielectric constant of the food such that microwave energy can be used to induce higher temperatures (Andrews, 1989).

2.4.2 Physical Property

Most foods heat in the microwave because the water in the product is excited by oscillation of the microwave field. Other factors effect heating such as product fat content, package geometry and product thickness.

For the nonpolar long chain fatty acids of fat and oil, the major effect is dependent on their specific heat (Shaath, 1988). The specific heat is defined as the amount of energy needed to raise product temperature by 1°C. The specific heat of fat and oil compared to water (sp. heat=1) is 0.5. The lower the specific heat, the greater the temperature increase of the food during microwaving (Shaath, 1988).

Package geometry affects heating of food in a microwave oven. Product edges and corners typically overheat, because the edges receive energy from two directions (top, side), and the corners get energy from three directions (top, two sides). This is one reason why microwave heating results in uneven heating patterns (Mudgett, 1989). The optimum shape for microwave heating of a container is spherical. In this design, there are no corners which will overheat, and the distance to the center of the product is minimized (Amini, 1988)

Product shape, mass and thickness also affect heating in the microwave. Circular shapes and thin portions heat more uniformly and avoid cool spots in the center. Product mass also affects heating time, larger mass requires longer heating times (Mudgett, 1989). Bones in meat can reduce the uniformity of microwave heating, because the calcium and other minerals reflect microwaves as they penetrate the muscle. Microwave heating takes longer at the bone surface than in other areas of the meat (van Zante,1973).

2.5 Types Of Microwave Packaging

There are essentially four different packaging materials designs used in microwave ovens. These include transparent, shielding, field modifying and absorbing (Perry, 1987).

2.5.1 Transparent Materials

Microwaves can penetrate through transparent material and interact with products inside the package. Consequently, the package material is heated indirectly by contact with the hot food. Product temperature is limited to 100°C (212°F) in the presence of liquid water. Once the water evaporates and is lost, product in corners and thin layers will dry out and become hot enough to melt polymers. Transparent polymers which can be used for microwave packaging material include : glass, polyethylene, polypropylene, polyester, nylon and paper products (Perry, 1987). These types of packaging materials are suitable for liquid foods such as sauce, vegetables, soups, etc.

2.5.2 Shield Materials

Shields are metallic structures that are thick enough to reflect microwaves, without causing heat generation. Shields are used to prevent microwaves from reaching a product or parts of a product, and also to control the direction of microwave penetration into a product. Shield material has been used in a multi-sectional meal tray which included a main meal and a dessert in the same tray (Keefer, 1986). Consumers can heat the main meal while the dessert remains cool. Shield material can be made from aluminum foil, foil laminated to a substrate, or any metal sheet fabricated into pans and trays.

There are two major problems associated with shields. First, there is large potential electrical build up on the shield material because it is a good conductor. When the area of potential comes close to a grounded surface or another shield material with different potential, an electrical discharge can occur (Fisher, 1990). Second, arcing between two shield material (or edges) may occur. A wave can be reflected from the corner or edge of a metallic surface, and cause damage to the magnetron (Perry, 1987).

Coating the foil with a non-conductive insulator, and heating product in metal pans while inside folding cartons can reduce the arcing problem (Perry, 1987).

2.5.3 Field Modification (Micro Match)

Field modification devices can modify electromagnetic fields to give (a) uniform heating (b) selective heating (c) browning and (d) prevention of arcing (Perry, 1987).

This system uses smoothwall lacquered foil containers, consisting of a composite dome made of plastic and aluminum. The microwave fields are modified into a higher order mode to focus and intensify microwave energy which can result in selective heating of product (Drennan, 1987). The aluminum array on the dome acts as an antenna, and focuses the microwave energy in proper frequency to the specific locations.

A field modification package can also be structured to cause browning or crisping by generating intense energy

fields on food surfaces. Unlike susceptors, field intensification does not cause increased temperature in the supporting structure since the cover (supporting structure) is separated from the surface of the food by an air gap (Keefer, 1986).

Field modification can also reduce uneven heating in microwave ovens by using the active component in the foil pan as a " mode-stirrer ". This promotes resonance in the microwave to allow better distribution of energy across the container. In figure 3 a comparison is shown of the maximum temperature differential between field modification (micro Match), microwave transparent and an unmodified foil container (Keefer, 1986).

2.5.4 Absorbing material (susceptor)

Susceptor materials are used to achieve browning and crisping of foods such as pizza, fish sticks, French bread, popcorn and other foods.

In a susceptor's most usual form, it consists of plastic film (PET) which has been metallized on one side, and laminated to paper or paperboard (Figure 4). The metal is usually aluminum which is vacuum metallized to the substrate (Andrews, 1989). The polyester provides a heat resistant substrate and is placed in contact with the food product. The plastic film can protect the aluminum from physical or chemical damage, and prevents aluminum from becoming an indirect food additive (Perry, 1987).

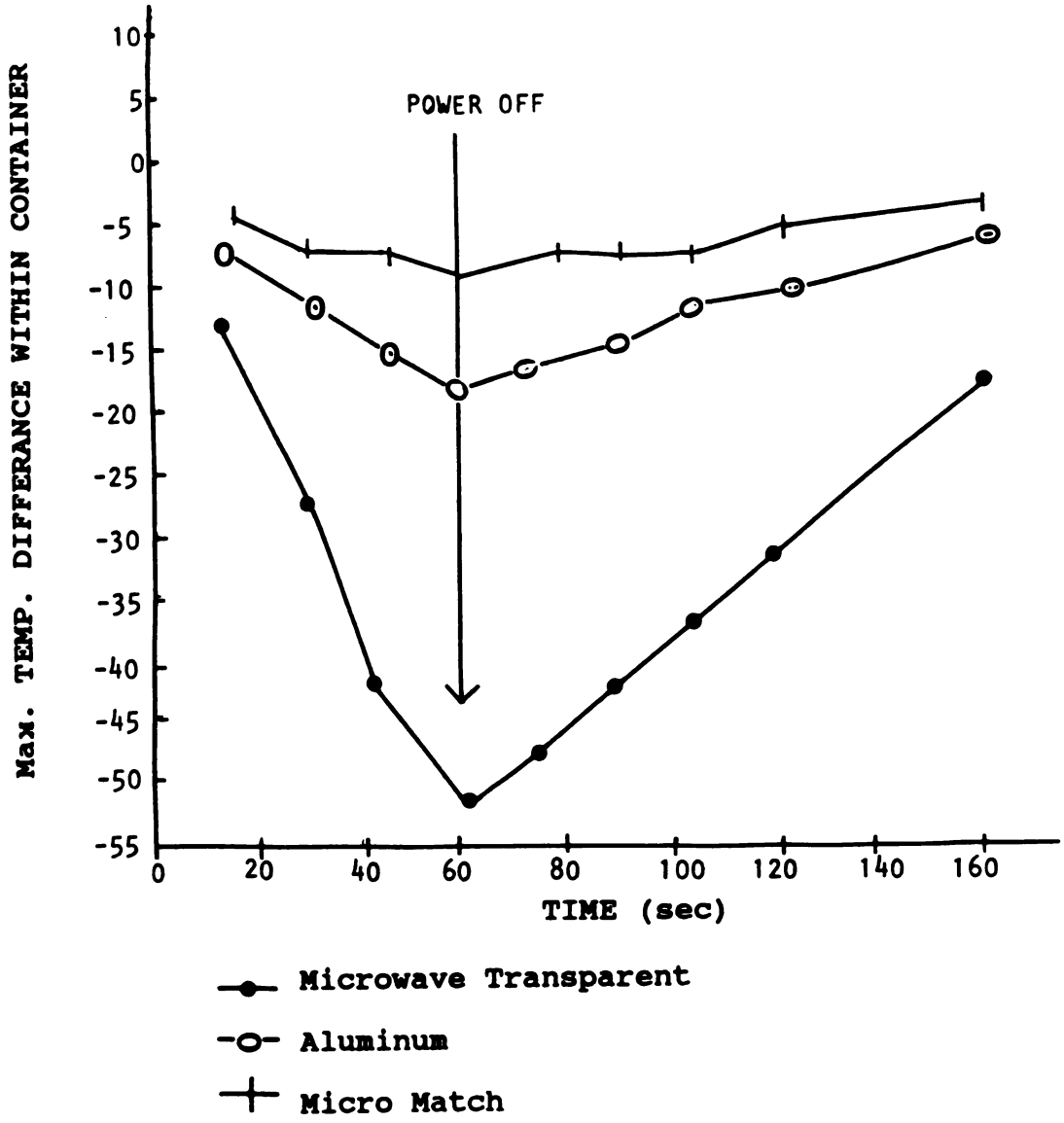

Figure 3. Time-temperature differentials between three microwave containers. (Keefer, 1986)

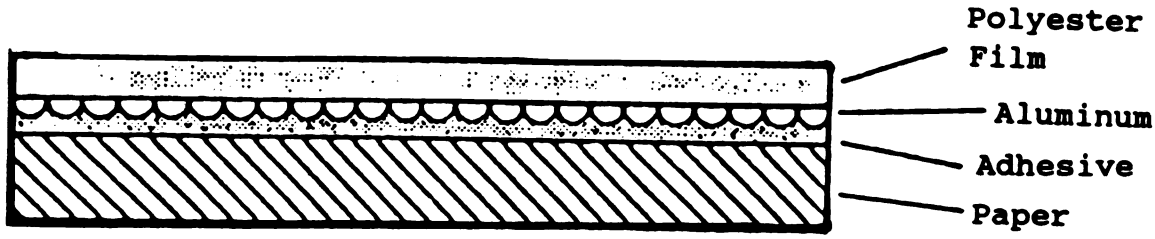

Figure 4. A cross sectional view of the susceptor material. (Anon, 1988)

The paper or paperboard provides mechanical support for the susceptor.

New developments in susceptor packaging include pressure-sensitive label forms, ULTEM® resin susceptor films, dual mode susceptors and flake-coated susceptors. Pressure-sensitive labels allow differential heating to occur within a package by precisely positioning the label in a food package (Anon,1989). ULTEM® resin has high heat resistance which can decrease the cracking and crazing of traditional susceptors (Stulga, 1989). The flake-coated susceptor is deposited at different levels by flaking aluminum onto PET film to modify the heat generated (Huang, 1987). The dual mode susceptor is designed to decrease uneven heating in microwaves by coupling to both the electric and magnetic fields in the microwave (Huang, 1987).

2.6 Interaction of Microwave with Susceptor

At present, two susceptor technologies have been developled for the microwave package market -- vacuum metallized aluminum and ferromagnetic coating (Rosenranz, 1987).

The metal (aluminum) coating absorbs microwave energy by coupling with the electric field component of the microwave radiation to produce the resistive heat. Through resistive heating in the thin film, the microwave energy is converted into sensible heat (Turpin, 1980). When the

packaging material warms up, the food is heated by conventional thermal conduction from the susceptor, thereby, promoting browning and crisping on the surface of the food product (Perry, 1987).

The ultimate temperature which the susceptor reaches is determined by the resistive heat. The resistive heat is dependent on the surface resistance (R_s) of the susceptor. The surface resistance (R_s) is defined in equation 3 (Ramey,et al., 1968).

$$R_s = \frac{1}{\sigma \cdot d} \qquad (3)$$

where R_s= surface resistance of susceptor (ohm/cm^2)
σ = film electrical conductivity (ohms/cm)$^{-1}$
d = film thickness (cm)

The relationship between resistance and microwave heating and susceptor design is shown in Figure 5 (Ramedy and Lewis, 1968). When the surface resistance is larger than 1000 ohms/cm^2, the susceptor becomes more transmissive and less absorptive and reflective. At the same electric conductivity, the larger R_s is provided by the thinner film. Electric field can easily penetrate thinner film and thus interact with the molecules of the susceptor to generate resistive heat. If the R_s is lower than 10 ohms/cm^2, the susceptor becomes more reflective, and less absorptive and transmissive. Thicker films have a smaller R_s, which means that it is difficult for the electric field to penetrate the

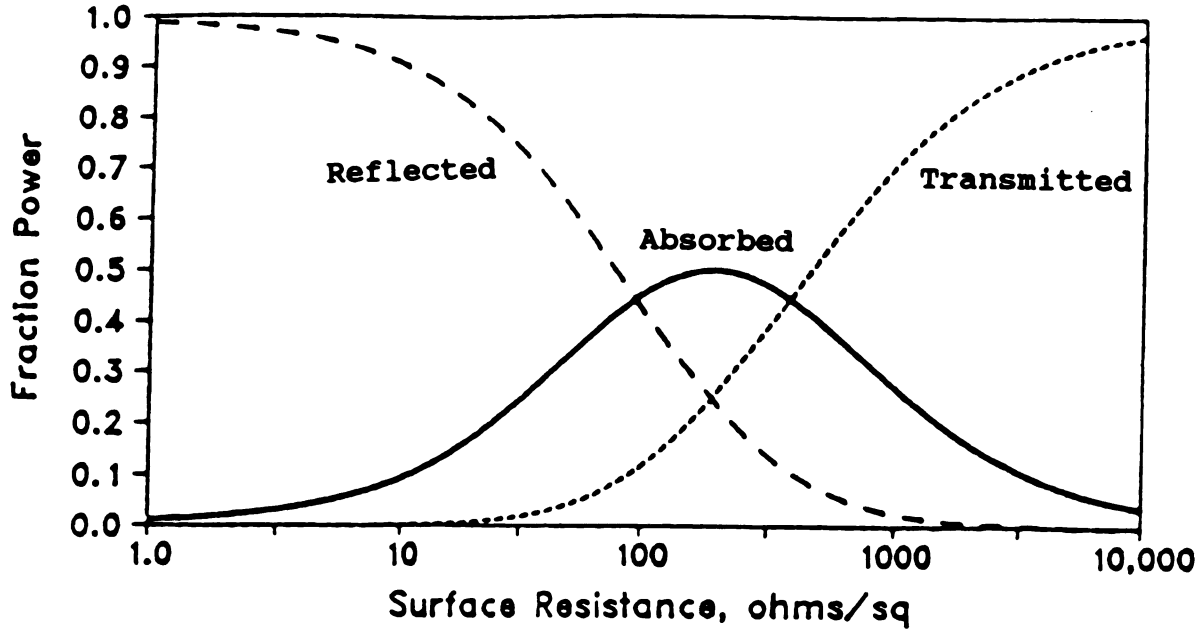

Figure 5. The surface resistance of susceptor and power absorption in different microwave heating characteristics (Pesheck, 1988)

thick film and interact with the molecules of the susceptor. For an absorptive susceptor, densities between 0.18 and 0.29 are best for crisping and browning. The Rs should be around 100 ohms/cm^2, and the thickness of aluminum should be between 60-100 Å (Pesheck, 1987).

Using vacuum metallized technology (aluminum), the susceptor couples only with the electrical field component of the microwave electromagnetic spectrum. The magnetic field strength maximum is always at the electric field minimum. Therefore, the traditional susceptor can not achieve uniform heat distribution.

Ferromagnetic films can also couple with the magnetic fields in the microwave region of the spectrum and generate heat during cycling of the magnetic field. Ferromagnetic materials enhance the interaction of incident magnetic energy within the microwave oven to achieve a desired cooking effect (Rosenkranz, 1987). At the end of cooking, the susceptor become transparent to the applied magnetic field, an only the electric field continues to heat (Rosenkranz, 1987). As result, the susceptor will not craze the material's surface due to overheating and result more uniformity in crisping and browning of the food.

2.7 Safety of Susceptors

Many microwavable packages incorporate susceptors to improve the eating quality of microwave food. Susceptors

promote uniform heating and selective browning/crisping. However, the susceptor may create localized package temperatures in excess of 500°F (Mitchell, 1988). No functional barrier exists between food and susceptor components, due to melting of the polyester film and browning of the paperboard (Mitchell, 1988). The Food and Drug Administration (FDA) held a public meeting on September 22, 1988 and described their concerns related to microwave susceptor packaging. They raised several questions (Hollifield et al., 1988) pertaining to susceptor packaging: (1) Do chemicals migrate from the food contact surface and into the food during microwaving? (2) Do temperatures encountered by susceptors during microwaving result in breakdown of the packaging materials? (3) Does the food contact layer protect the product from potential migrants within the packaging materials? These issues have led to government, industry and university sponsored research to generate data on maximum use time/temperature conditions, breakdown products of packaging material during high temperature use and migration of components from the material into foods.

The FDA requires pre-market approval for products where additives may become part of any food product, (Code of Federal Regulations (CFR) title 21 and CFR 170-186), see table 3. The FDA did not anticipate the extreme temperatures that these materials would reach during

Table 3. Federal regulations on food packages and package components.

Code of Federal Regulations Citation	Topic
21 CFR Part 170	Food additives
21 CFR Part 174	Indirect food additives: general information
21 CFR Part 175	Indirect food additives: adhesives, coating and component
21 CFR Part 176	Indirect food additives: paper and paperboard component
21 CFR Part 177	Indirect food additives: polymers
21 CFR Part 178	Indirect food additives: adjuvant, product aid,sanitizer
21 CFR Part 179	radiation in production, processing and handling of food
21 CFR Part 181	Prior-sanctioned food ingredients
21 CFR Part 182	Substances Generally Recognized as Safe (GRAS)
21 CFR Part 186	Indirect food substances affirmed as GRAS

Source: Risch, 1988

microwave use (Risch, 1988). The regulation is inadequate as a test for susceptors. For example, CFR 175 requires a functional barrier between a food product and an adhesive, but it doesn't test for the volatile and non-volatile additives which may result under high temperature use. CFR 176 does not set temperature limits for the paper and paper components. CFR 177 allows laminated polymers in direct food contact, but only up to 275°F (Risch, 1988). In the absence of appropriate data it is impossible to fully evaluate the safety of susceptors in such high-temperature uses.

2.8 Theory of Migration

Migration is described as the transfer of substance from a packaging material into a food product. Substances include volatile and non-volatile components. Volatile species may desorb and evaporate from the surface of the packaging material into the surrounding atmosphere, and be reabsorbed by the food product. The non-volatile elements may diffuse from the surface of the packaging material where they are reabsorbed in direct contact with products possessing specific affinity for the components.

Migration is basically a desorption process which depends on the diffusivity of the species in the polymer. Diffusivity, or diffusion coefficient (D), is defined as the tendency of a substance to permeate through the polymer bulk

phase. The driving force is dependent upon a concentration gradient, where the dissolved species diffuses from a high concentration region to a low concentration area (Giacin, 1980). The rate of diffusion is defined by Fick's first law:(Crosby, 1981)

$$\frac{dm}{dt} = -D \cdot A \frac{dc}{dx} \qquad (4)$$

where m = mass of the component transferred
t = time
c = migrant concentration
x = path of diffusion
D = diffusion constant
A = area of plane across which diffusion occur

If the diffusion process is over an infinite surface (i.e., a sheet), the mode of migration probably follows Fick's second law and is shown below:

$$\frac{dc}{dt} = D \frac{d^2 c}{dx^2} \qquad (5)$$

In this expression, the diffusion coefficient is constant and independent of the concentration (equation 5). Hence, for steady state diffusion with a fixed concentration gradient, Fick's law relates the concentration to a function of time, temperature and product affinity (Crosby, 1981).

There are three potentially different migration situations: (1) nonmigrating; (2) independently migrating; and (3) leaching (Briston and Katon, 1974). In the nonmigrating system, migration occurs only from the packaging surface with essentially zero diffusion. In the

independently migrating system, diffusion take place as the component evaporates from the surface of the polymer and is replaced by similar components diffusing through the material. The diffusion coefficient is measured under the time-temperature conditions of the study. For many volatile compounds and solid additives, system two is likely. The rate of migration and amount of migrant transferred will be dependent on the contact phase volume, boundary layer resistance in the extracting phase and the time scale for desorption (Giacin, 1980). During leaching, components of the contacting phase interact with the polymer and cause swelling which can increase the diffusion of non-volatile migrants (Crosby, 1981). As the package temperature increases, swelling of the packaging material may occur and accelerate diffusion and evaporation of both volatile and nonvolatile components (Giacin, 1980).

Migration of indirect additives from packaging materials to food are regulated either as global migrants or specific migrants. Global migration refers to the total transfer or migration of all components from the material to product regardless of whether they have potential toxicity. Specific migration relates to a specific individual component which is a constituent of the packaging material. The limits of specific migration are defined by compounds known or regarded as possibly hazardous to human health (Giacin, 1980).

2.9 Analytical Method and Study for Volatile Migration

A substantial amount of research has been done in the area of migration of substances from packaging materials into foods. Whitney and Collins (1978) and Varner (1983) determined the migration of monomers and low molecular weight residues from plastic film. Bieber (1984) studied the migration of low molecular weight additives from HDPE, LDPE and PP into food. Schowpe (1987) conducted studies on migration of antioxidants, and Hotchkiss and Landois-Garza (1987) determinated migration of aroma and flavor compounds from packaging materials into food. Kozyrod and Ziaziaris (1989) reviewed the migration of plasticizers into food.

2.9.1 Migration Study -- Microwave Heating

Limited research has been done to investigate the migration of monomers and volatiles from microwave cookware during microwave heating. Migration of acetyl tributyl citrate (ATBC) from plastic film into poultry products during microwave cooking was studied by Heath and Reilly (1981). After microwave heating for 8 minutes, they compared the infrared spectrum of the film used to cover the chicken to that of unused film . They reported that the amount of ATBC in the poultry meat increased as the microwave heating time increased. Using a model food system, they found that by increasing the lipid portion of the product more plasticizer migrated during microwave heating.

Bishop and Dye (1982) studied the migration of the plasticizer, di-(2-ethylhexyl) adipate (DEHA), from a plastic wraping material after 10 minutes of exposure in a microwave oven. They trapped the migrants using vegetable oil, and analyzed the oil by gas chromatography to get 33.35 mg/dm^2 of DEHA released from the plastic wrap. Startin et al., (1987) also studied the migration of DEHA from a flexible packaging film (PVC) into a variety of foods during microwave cooking. Migration occurred and was highest for meat (351 mg/kg for pork spare ribs) and lowest for vegetables (3 mg/kg for carrots). They concluded that migration increased with increased contact time, temperature and fat content of food.

2.9.2 Volatile Migrants from Microwave Packaging

Volatile compounds diffuse quickly, therefore, it is important that they are identified and quantified so that the safety and utility of the containers can be determined. Dixon-Anderson et al. (1988) used a plastic coextruded cup (PP/Saran^R/PP) to demonstrate the loss of volatiles from cup material. Strips of the material were microwaved in sealed glass vials for periods from 3 to 7 minutes. After heating, the headspace of the vials was sampled and analyzed using a flame ionization detector (FID) gas chromatography. Five major peaks were detected and quantified in the headspace (Figure 6). Using mass spectrometry , the five components were identified as hydrocarbons and butylated hydroxytoluene

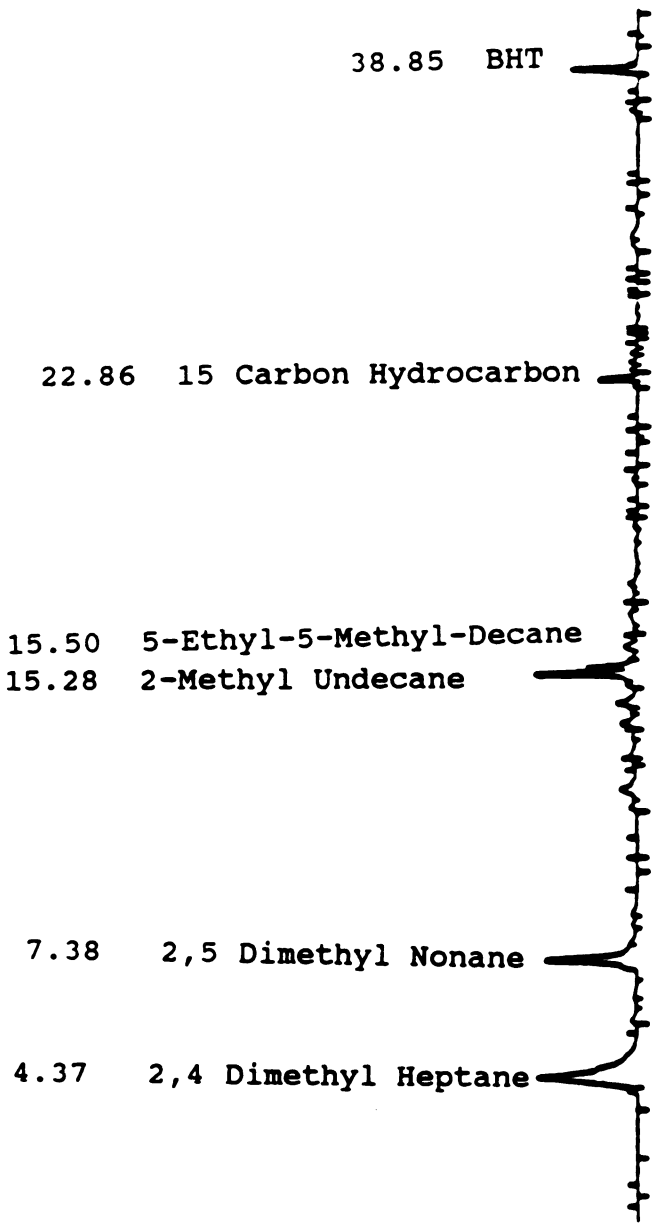

Figure 6. Chromatogram of volatiles released from the container material during microwaving. (Dixon-Anderson et,al., 1988)

The quantity of each component increased with increased microwaving time. The release of organic compounds from material may be a near-the-surface phenomenon since the middle layer (PVDC) did not appear to have contributed to the pool of volatiles in the headspace.

2.9.3 Volatile Migration of Susceptors

Although no regulations pertaining to migration of volatile components from susceptor materials have been reported to date, FDA developed a preliminary test using the headspace method (Hollified,et al., 1988). In this study, a susceptor was put in a headspace vial and microwaved at full power for 2 minutes. An aliquot of the headspace gas was then injected into the gas chromatograph (GC) for analysis. The susceptor volatiles identified are listed in Table 4. The table also shows compounds found in corn oil extracts which was in contact with a susceptor tray microwaved at full power for 3 minutes. The furfural and various alcohol compounds could be components of the adhesive layer or breakdown products of paper or adhesive.

To determine volatile migrants from a susceptor package, Booker and Friese (1989) used diffusion trapping and headspace methods to determine migration of volatiles during microwave heating and conventional heating. For headspace analysis, the sample was prepared in a manner simular to the FDA'S method (1988). In the diffusion trapping method, the susceptor was cut into 0.02 g samples

Table 4. Volatile chemicals from susceptor materials and those identified or confirmed in corn oil

Found in Susceptor	Identified in Oil Extracts	Confirmed as Migrant
aceton		
benzene		
1-hexanal		
2-furfural	Yes	Yes
2-butoxy-1-ethanol	Yes	Yes
benzaldehyde	Yes	
2-furfurol	Yes	Yes
2-methyl propanol	Yes	Yes
n-butanol	Yes	Yes
styrene		
2-ethyl-1-hexanol		
isopropanol		
xylenes		
toulene		

Source : Hollfield, 1988

and put into a glass vial along with a Tenax-GC trap. The vials were sealed and heated both in a microwave and conventional heating, and then equilibrated at 40°C for sixteen hours. The Tenax was transferred to a GC liner and purged into the GC column using a carrier gas.

In the headspace procedure, there was good correlation between the two different heating processes. In the diffusion trapping procedure, no volatiles were absorbed by the Tenax during microwave heating, however, volatiles were absorbed on the Tenax using a conventional heating process. In microwave heating, the sample temperature (120°F) was much lower than what a susceptor would actually see during cooking of a frozen microwavable pizza (around 400°F) since the sample size was too small (0.02 g). In a conventional heating process, the sample temperature can reach 400°F using an oil bath to generate the migration of volatiles. The results showed that a valid test procedure could be designed using conventional heating rather than microwave radiation to quantity the volatiles.

Also there were two classes of volatiles released during heating : thermally desorbed compounds and pyrolysis products (Table 5). The thermally desorbed compounds were indigenous elements of packaging materials, such as residual chemicals from the papermaking process, solvents from adhesives and contaminants. The other classes are products produced from pyrolysis of paperboard, coating, inks,

Table 5. Volatile products released from susceptor material during microwaving

Thermally Desorbed	Pyrolysis Products
Papermaking process	Pyrolysis of paper
. 1,1,1-trichloroethane	. furfural
. toluene	Pyrolysis of polymer
. aliphatic hydrocarbons	. styrene
. xylene	
. naphthlene	
. methylene chloride	
. fluorocarbons	
. styrene	
Adhesive	
. 2-butoxy-1-ethanol	
. alcohol	
. toluene	
. 1,1,1-trichloroethane	
Contamination	
. WD-40	

Source : Booker and Friese, 1989

varnishes, etc. Heating for long times at the desired temperature would result in new compounds formed as the package material reaches the degradation temperature.

Rousselo (1990) determined the volatile migrants from a susceptor using the diffusion trapping and headspace procedures. Susceptor board was cut to a specific sample size and sealed into glass vials. In the headspace method, the sample was heated at full power with water loading for time periods ranging from five to seven minutes, and then an aliquot of the headspace volume was removed and analyzed using GC. For diffusion trapping, Tenax was enclosed with the sample in a vial and then heated in a hot oil bath at temperatures ranging from 200 to 240°C for five minutes. After equilibrating, the Tenax was placed into a liner preceding the GC column. Material temperature was monitored in the oil bath using a thermocouple and Luxtron probes in the microwave oven. Diffusion trapping was more sensitive than the headspace technique. The presence of water in the microwave decreased the temperature of the susceptor sample which caused a decrease in the amount of volatiles desorbed. There were six major components identified using mass spectroscopy: 2-methyl propanol, n-butanol, styrene, 2-butoxy-1-ethanol, furfural and 2-(2-butoxyethoxy)ethanol (Figure 7).

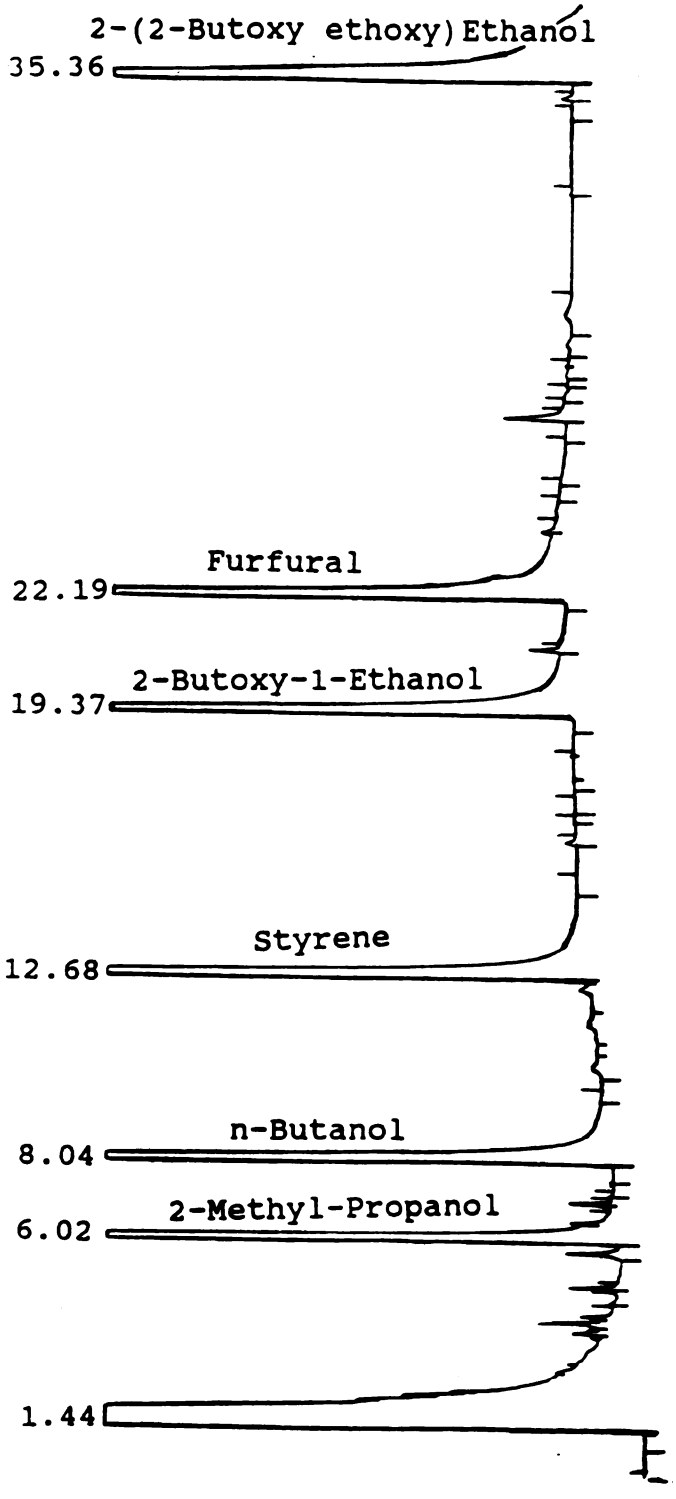

Figure 7. Chromatogram of volatiles released from the susceptor material during microwaving. (Rousselo, 1990)

2.9.4 Dynamic Thermal Stripper as a Method for the Migration of Volatiles

The traditional static headspace method of analysis allows only a relatively small volume of gas above the sample to be injected through a syringe (headspace procedure) or sorbant packed trap(diffusion trapping) onto a GC column. The reproducibility of the headspace method is poor, because the slight deviations in temperature, pressure, sample matrix or injected volume may cause drastic changes in the headspace composition. For the diffusion trapping procedure, it takes a long time (at least 16 hours) to absorb the volatiles by the sorbet materials (Tenax).

In the dynamic thermal stripper method, the sample is put into a glass vial, and the vial is connected into the oven of a thermal stripper instrument. The carrier gas continually sweeps the volatiles from the sample to go through the sorbet tube. The sweep cycle is continued until all of the volatiles are collected by the sorbet materials, thereby, increasing the concentration level many times over the static headspace analysis. After thermal stripping,the sorbet tube is positioned in the thermal desorption unit. During thermal desorption, the tube is heated to desorb the volatiles and carrier gas passes through the tube into the GC column to analysis (Supleco co., 1989).

The sorbet materials used to collect volatiles are an important factor contributing to the trapping and desorption

efficiency. A good combination of adsorbent materials to use in the stripper is: Tenax-TA, Carbotrap B and Carbotrap SIII (Supelco co., 1989). These are packed in layers in the sorbet tube. The higher molecular weight volatile compounds are adsorbed on the Tenax layer. Because the Tenax particles are larger (35/60 mesh) than Carbotrap compounds, the higher molecular weight compounds can be trapped inside the Tenax. The smaller molecules pass through the Tenax and are absorbed on the carbotrap and/or carbosieve layers. Since each molecular weight range is trapped on an appropriate sorbet materials, the volatiles are easily released from the sorbet tube using the desorption unit. Nothing is held so tenaciously that it decomposes during desorption, therefore, the dynamic thermal desorption technique is more sensitivity and reproducibility than the static headspace method.

CHAPTER 3

MATERIALS AND METHODS

3.1 Susceptor

The susceptor material was provided in sheet form (0.61 m x 0.91 m) by a food company. This material was composed of metallized (aluminum) polyethylene terephthalate (PET), laminated to paperboard.

3.2 Headspace Method for Releasing Volatile Compounds

The headspace analysis was based on the ASTM Committee F-2.3 (1990) recommended method, and a modification of the procedure of Rousselo (1990).

3.2.1 Microwaving Heating

A 10 mm x 65 mm sample of susceptor material was weighed and put into a 35 ml glass vial face upward. A 20 mm conditioned teflon/silicone septum (Supelco Co., Bellofont, PA) was placed over the vial with the teflon side toward the vial, and crimped shut with an aluminum cap which covered the septum. The septa were conditioned by irradiating at full power in a microwave for 10 minutes, following by heating under 30 in-Hg in a vacuum oven (Model 524, Precision Scientific Co., Chicago, IL) at 130°C for at least 16 hours.

The sealed crimp cap vial was placed into the microwave oven (Amana Radarange, 700 watt Model RR1010, Amana Refrigerator Inc., Amana, IA) without water loading, at the center of the oven. Susceptor material samples were heated at full power for 1, 2, 3, 4 and 5 minutes respectively, in the microwave oven.

Following radiation, the vial containing the sample was placed along with a 1000 µl gas tight syringe (# 1001, Hamilton Co., Reno, NV), into a 90°C hot air oven (Model 18, Precision Scientific Co., Chicago, IL), and allowed to equilibrate for 5 minutes. After equilibration, the vial and syringe were removed from the oven. The syringe was filled with 1 ml of air and injected into the vial. An aliquot of headspace (0.5 ml) was drawn back into the syringe and injected into the vial twice. A 1000 µl sample was taken from the vial and injected into a Hewlett Packard Model 5890A gas chromatograph (GC) equipped with dual flame ionization detectors (FID). Four replicates were accomplished for each of the heating times.

3.2.2 Oil Bath Heating

A 10 mm x 65 mm sample of susceptor material was cut in half and put in a 40 ml vial with a teflon-lined septum screw cap (22 mm, Pierce Co., Rockford, IL). The 40 ml screw cap vial was used to accommodate removal of the Tenax. The sealed vials were heated in an oil bath at a specific temperature for 1, 2, 3, 4 and 5 minutes, respectively. The

oil bath temperatures were set at 180, 200 and 220 ± 1°C.

The vial was then removed from the oil bath and equilibrated along with a 1000 µl gas tight syringe in an air oven at 90°C for 5 minutes. After equilibration, the vial and syringe were removed. A 500 µl headspace sample was withdrawn from the vial with the gas tight syringe, and injected into a Hewlett Packard 5890A GC equipped with dual FID detectors. Four replicates were performed for each heating time at each temperature.

3.3 Diffusion Trapping Method for Releasing Volatile Compounds

A diffusion trapping technique (Booker, 1985, 1989) was used to measure the volatiles released from the susceptor material.

3.3.1 Tenax GC® Conditioning

Tenax GC® (poly-(2,6-diphenyl-ρ-phenylene oxide), 35-60 mesh) was obtained from Alltech Associate Inc., (Deerfield, IL). Tenax GC was packed into a glass chromatoghaphic column (20 m x 50 mm ID). The column was then connected to the injection port of a Hewlett Packard Model 5830A gas chromatograph equipped with a flame ionization detector (FID). During the conditioning step, the column was disconnected from the detector.

The GC oven temperature was programmed to condition the Tenax as follows: the initial temperature was set at 50°C

for 40 minutes, the temperature was then increased at a rate of 1°C/min until the final temperature of 240°C was attained. The GC was then held at 240°C for 10 hours. The injection port temperature was maintained at 175°C and the flow rate of helium through the column was 40 ml/min.

After conditioning, the Tenax was poured into a 40 ml glass vial and the vial closed with a screw cap. The vial was then stored at 21°C until needed. Before using the Tenax as a sorbant in the diffusion trapping method, it was necessary to check the GC signal background of Tenax using the same GC conditions developed for the analysis of the headspace volatiles (see section 3.5).

3.3.2 Sample Preparation

A disc of susceptor (10 mm diameter) material was cut from the sheet, weighed and placed into a 40 ml glass vial fitted with a teflon-lined septum cap. A 12 mm x 75 mm disposable culture tube (Kimax® 51, VWR Scientific, Inc., San Francisco, CA) containing 0.03 ± 0.005 g of conditioned Tenax GC was placed into the tube so that it rested on top of the susceptor disc. The vial was sealed and placed in an oil bath, as shown in Figure 8 (Rousselo, 1990). Susceptor samples were heated in the oil bath at 180, 200 and 220 ± 1°C. For each temperature, heating times of 1, 2, 3, 4 and 5 minutes were selected to release volatiles from the material.

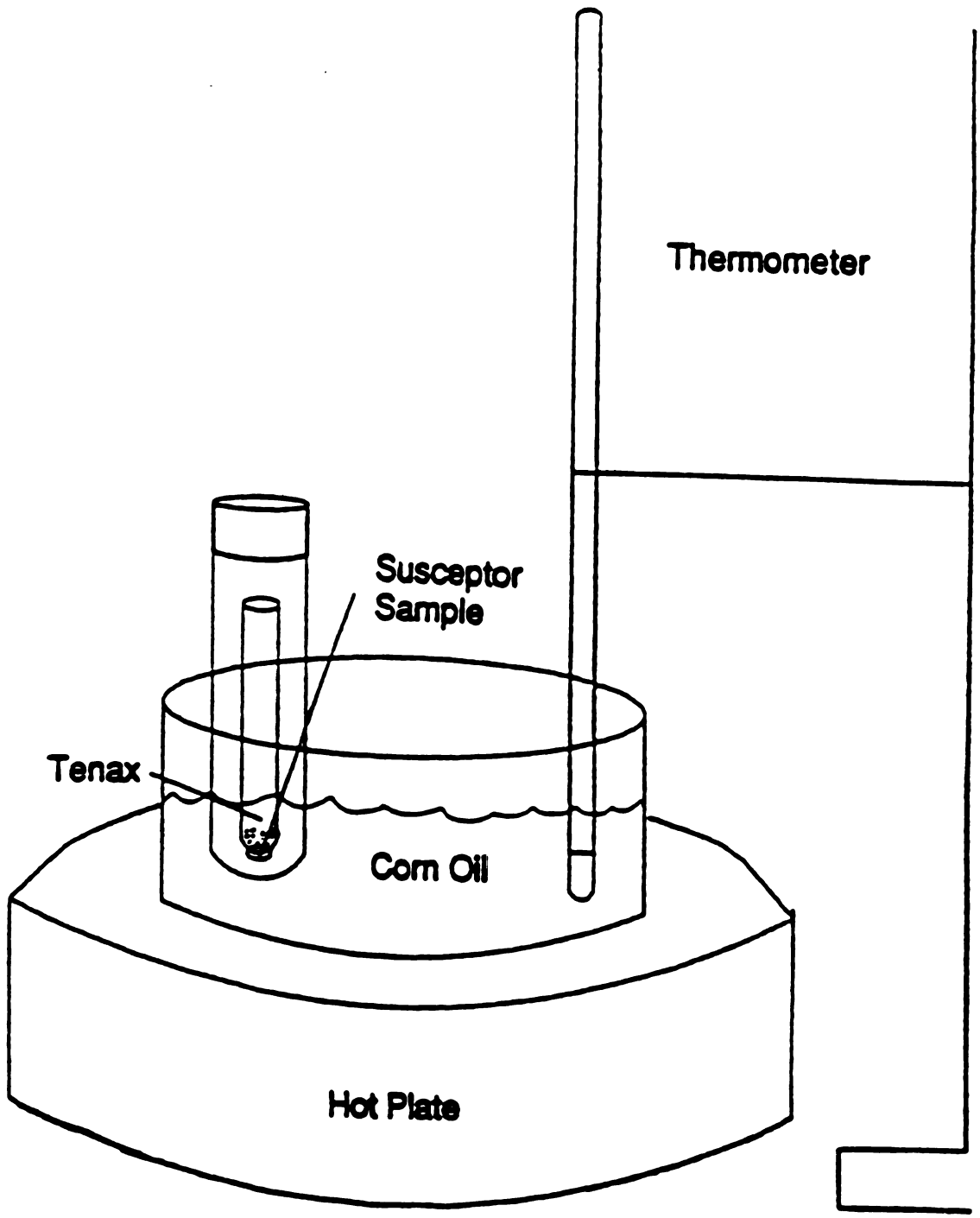

Figure 8. Schematic of diffusion trapping technique. (Rousselo, 1990)

After conventional heating of the sample, the vial and its contents were placed into an air oven at 45°C for at least 16 hours. The Tenax in the culture tube was then transferred to an injection port liner tube and the liner tube placed into the injection port of the GC. The Tenax was retained in place by glass wool plugs on both ends of the liner. Using a toggle switch to shut off the gas flow, the injection port of the GC was quickly opened, and the liner containing Tenax inserted. The injection port was closed without delay and carrier gas flow resumed. The chromatographic analysis of volatile compounds was generated using a Hewlett Packard 5890A GC with flame ionization detector. Four replicates were done at each heating time for 180, 200 and 220°C.

3.4 Thermal Desorption Method for Releasing Volatile Compounds

3.4.1 Sample Preparation -- Thermal Stripper Procedure

A sample of the susceptor (50 mm x 130 mm) was randomly cut from a sheet. The sample was weighed (0.02 ± 0.001 g) and placed into a 20 ml sparging vial (Supelco Co., Bellefonte, PA). The vial was put into the oven of the thermal stripper instrument (Model 1000, Dynatherm Analytical Instruments, Inc. Kelton, PA), and connected to a sorbant tube which was positioned outside of the oven. The sorbant tube containing Carbotrap™ 300 Multi-bed materials,

(Supelco Co., Bellefonte, PA) was covered with a sleeve heater (Figure 9).

The thermal stripper conditions were set to heat samples at 180, 190 ± 1°C. When the sample temperature were set at 180°C, the block temperature was 190°C and the collection tube temperature at 90°C. Based on the preheat time setting, it required 6 minutes to increase the sample temperature to 180°C. The sample was then purged for 1, 2, 3, 4 and 5 minutes to drive the volatiles to the sorbant tube. After purging the samples, 4 minutes of drying time were selected to sweep any residual water vapor from the sorbant tube. The carrier gas (helium) pressure was maintained at 40 psi. The flow rate through the sample and block tube was set at 75 ml/min during purging, and 36 ml/min through the block tube during the drying step. Three replicates were performed for each of the purge times.

When the sample temperature was set at 190°C, the block temperature was 195°C and the collection tube temperature was 92°C. A preheating time of 8 minutes was necessary for the oven to attain 190°C. The other settings remained as previously described.

3.4.2 Volatile Desorption -- Thermal Desorption Unit

After sample preparation, the sorbent tube was taken from the thermal stripper and put into the tube chamber of the thermal desorption unit (Model 890, Dynathermal Analytical Instrument, Inc., Kelton, PA). There are two

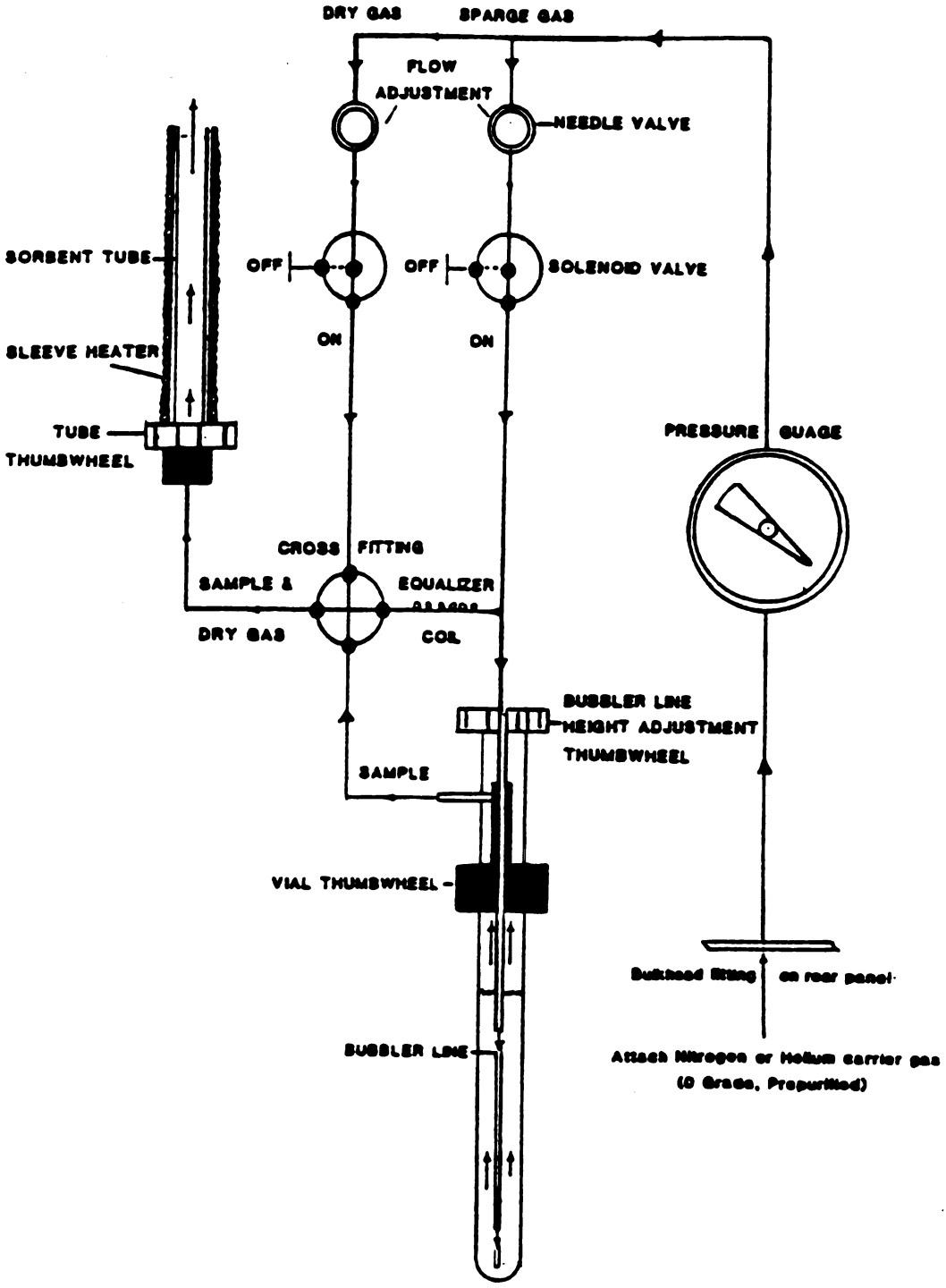

Figure 9. Carrier gas flow schematic of thermal stripper.

(Supelco, 1989)

flow paths used in the thermal desorption unit (Figure 10). Flow path A was used to desorb the compounds from the sorbant tube to the side port. Flow path B was used to thermally desorb the compounds collected on the sorbant tube and transfer them to the GC column for analysis. The volatiles from the susceptor were desorbed by path B for 4 minutes at 350°C. The transfer line was set at 260°C and the valve tube at 230°C to maintain the compounds in the vapor phase while being transferred to the gas chromatograph. Helium was used as the carrier gas and the flow rate was 2.96 ml/min at 40 psi through the thermal desorption unit.

After sample desorption, the sorbant tube was conditioned in path A in the thermal desorption unit prior to reuse. The temperature of the unit was set at 340°C for 30 minutes. The flow rate of helium gas through the sorbant tube to the side port was 10.71 ml/minutes at 40 psi.

3.5 GC Analysis of Volatile Compounds

The GC conditions used to determine release of volatile compounds for the above three methods were as follows: a fused silica capillary column (30 m x 0.32 mm ID) polar bonded stationary phase Supelcowax™ 10 (Supleco Co., Bellefonte, PA) with a helium carrier gas flow rate of 2.21 ml/min was used to seperate the compounds. To evaluate the sample, the GC was temperature programmed. The initial

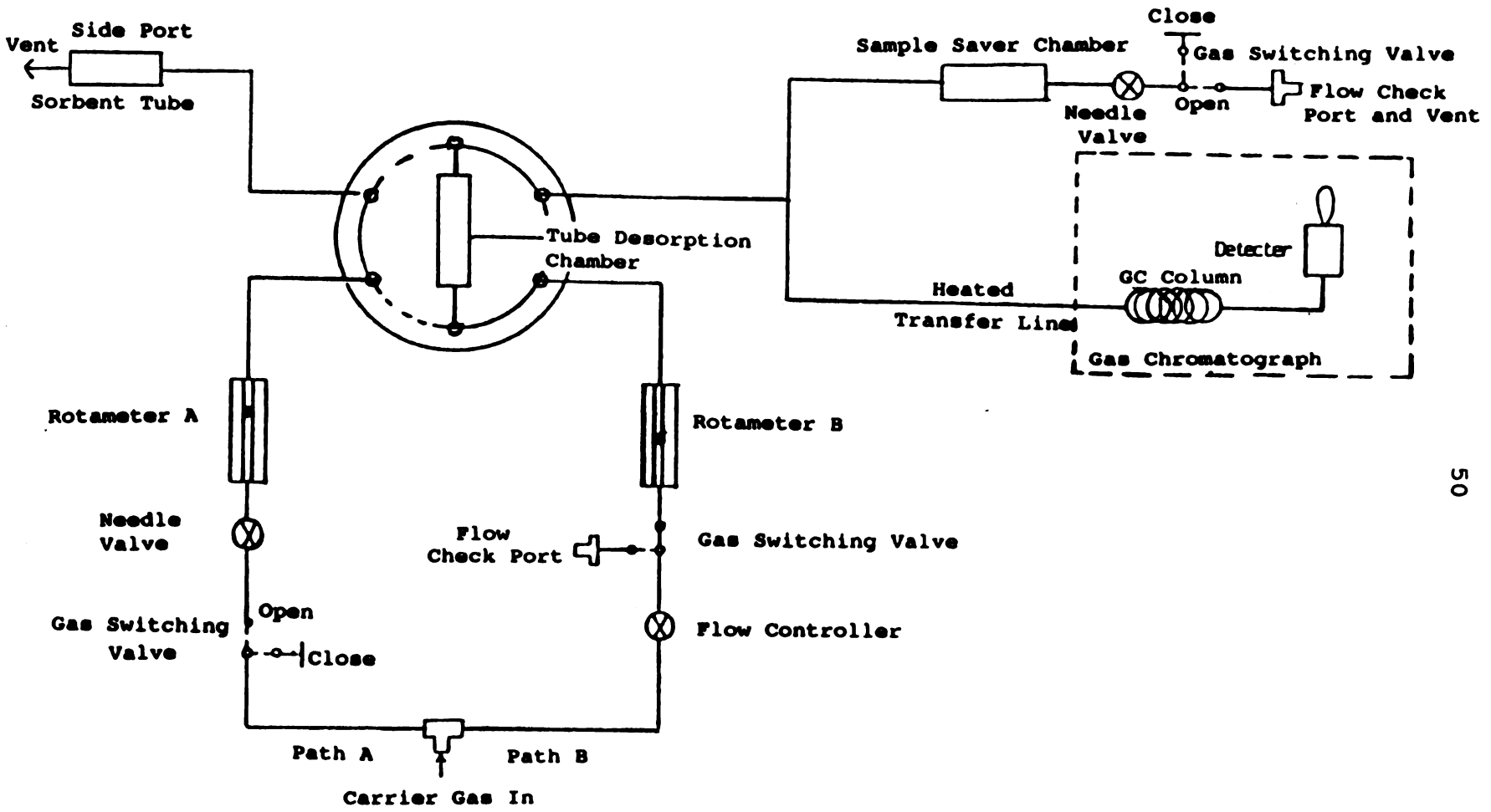

Figure 10. Carrier gas flow schematic of thermal desorption unit. (Supelco, 1989)

temperature was maintained at 40°C for 5 minutes, and then increased to 165°C at the rate of 2°C/min. The oven temperature was held at 165°C for 5 minutes. The temperature of the injection port was set at 180°C and column head pressure was maintained at 11 psi (0.77 kg/cm^2). The retention times of the six probe compounds are described in results and discussion section (pages 55, 69 and 81). All injections were executed using a splitless injection port.

3.6 Calibration Curve for Quantification

3.6.1 Calibration Curve Using in the Headspace Technique and Diffusion Trapping Method

Calibration curves for the six probe compounds were constructed to determine the linearity and sensitivity of the method. The probe compounds selected for quantification were n-butanol, 2-methyl propanol, styrene, 2-butoxy-1-ethanol, furfural and 2-(2-butoxyethoxy)ethanol. These compounds were 99+ % purity, and all were purchased from Aldrich Chemical Co. (Milwaukee, WI). Liquid standards of concentrations 10, 50, 100, 200 and 400 ppm (wt/v) were prepared using hexane (HPLC grade, Fisher Scientific Co., Fair Lawn, NJ) as the solvent. A 0.5 µl sample of each standard solution was injected into the gas chromatograph for analysis using a 10 µl syringe (#701, Hamilton Co., Reno, NV). The GC conditions were the same as listed

previously. Four replicates were performed at each concentration. The standard curves were constructed to relate peak area of analyte to its absolute quantity. The external standard curves were used to quantify the volatiles released from the susceptor material, using both the headspace and diffusion trapping methods.

3.6.2 Calibration Curve Using in the Thermal Desorption Method

Solvent can not be used on the thermal stripper instrument because the solvent will overload the sorbant tube and reduce the absorptive capacity available. Calibration curves for all six compounds (2-methyl propanol, butanol, styrene, 2-butoxy ethanol, furfural and 2-(2-butoxy ethoxy)ethanol) were therefore constructed using a headspace technique as follows: different volumes were withdrawn from standard solutions of the compounds and injected into 120 ml vials to obtain specific concentrations (wt/v). The concentrations ranged from 1 ppm to 83 ppm (wt/v), depending upon the specific standard solution. A conditioned teflon/ silicone septa (20 mm) was placed over each vial with the teflon side toward the vial, and covered with an aluminum cap and crimped close. Each vial was equilibrated at 21°C which allowed the standard solution to evaporate completely into gas phase. For the high boiling 2-(2-butoxyethoxy) ethanol (231°C), the vial was maintained at 100°C to assure complete volatilization. Septa and vials were conditioned

by heating at 130°C for 24 hours in an air oven to reduce the possibility of contamination from the septa and vials.

A 50 µl headspace sample was removed from each 120 ml vial and injected into the 20 ml sparge vial of the thermal stripper instrument using the Carbotrap 300 sorbant tube to absorb the volatiles. The conditions employed with the thermal stripper varied for each standard compound (Table 6) to obtain maximum efficiency. The sorbant tube was removed from the thermal stripper and put into the tube chamber of the thermal desorption unit (TDU). The volatiles were then desorbed directly onto the GC column for analysis. The TDU conditions were the same as previously described. Three replications were performed for each concentration.

Table 6. Conditions of thermal stripper instrument for six standard compounds

Compound*	A	B	C	D	E	F
boiling point (°C)	108	118	146	171	162	231
preheat time (min)	2	2	2	3	3	5
purge time (min)	7	7	7	7	7	7
dry time (min)	4	4	4	4	4	4
block temp.(°C)	145	145	145	180	180	190
oven temp.(°C)	50	50	50	90	90	150
tube temp.(°C)	45	45	45	65	65	90

* Compound A: 2-methyl propanol

Compound B: n-butanol

Compound C: styrene

Compound D: 2-butoxy ethanol

Compound E: furfural

Compound F: 2-(2-butoxyethoxy)ethanol

CHAPTER 4

RESULT AND DISCUSSION

4.1 Headspace Technique

4.1.1 Microwave Heating of the Susceptor

The six probe compounds selected for quantification had retention times of 5.41, 7.20, 11.70, 18.64, 21.03 and 35.34 minutes, respectively, and were 2-methyl propanol, n-butanol, styrene, 2-butoxy ethanol, furfural and 2-(2-butoxyethoxy)ethanol. The quantities of the volatiles released following heating of the susceptor in the microwave oven are shown in Table 7. The levels of volatiles released from the susceptor as a function of heating in the microwave from 1 to 5 minutes are shown in Figure 11.

The quantitation of volatiles can not be extrapolated from one heating time to another, as Figure 11 illustrates. After 1 minute of radiation, the level of volatiles significantly increased. From 2 to 4 minutes heating time the quantity of volatiles was found to increase at a much lower rate. The quantity released did not increase linearly with time. Quantitation of the volatiles released from 1 to 4 minutes heating and extrapolation to longer times will result in underestimation of the amount of volatiles likely to be generated. As the heating time was increased to

Table 7. Volatiles from the susceptor material during microwave radiation using a headspace technique.

Time (min)	Quantity (μg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	20.32±2.41	4.88±0.74	0.40±0.12
2	19.31±1.56	7.27±1.44	0.45±0.13
3	21.31±2.13	10.97±1.66	0.71±0.22
4	19.04±0.96	11.76±2.31	0.64±0.17
5	25.23±3.86	20.67±2.74	1.11±0.26

Time (min)	Quantity (μg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.16±0.12	12.54±5.41	10.26±2.48
2	0.72±0.36	27.64±9.34	12.94±3.10
3	0.80±0.19	28.97±6.66	14.06±4.89
4	0.87±0.33	35.76±7.98	16.07±5.68
5	2.51±0.46	70.06±10.77	28.92±9.73

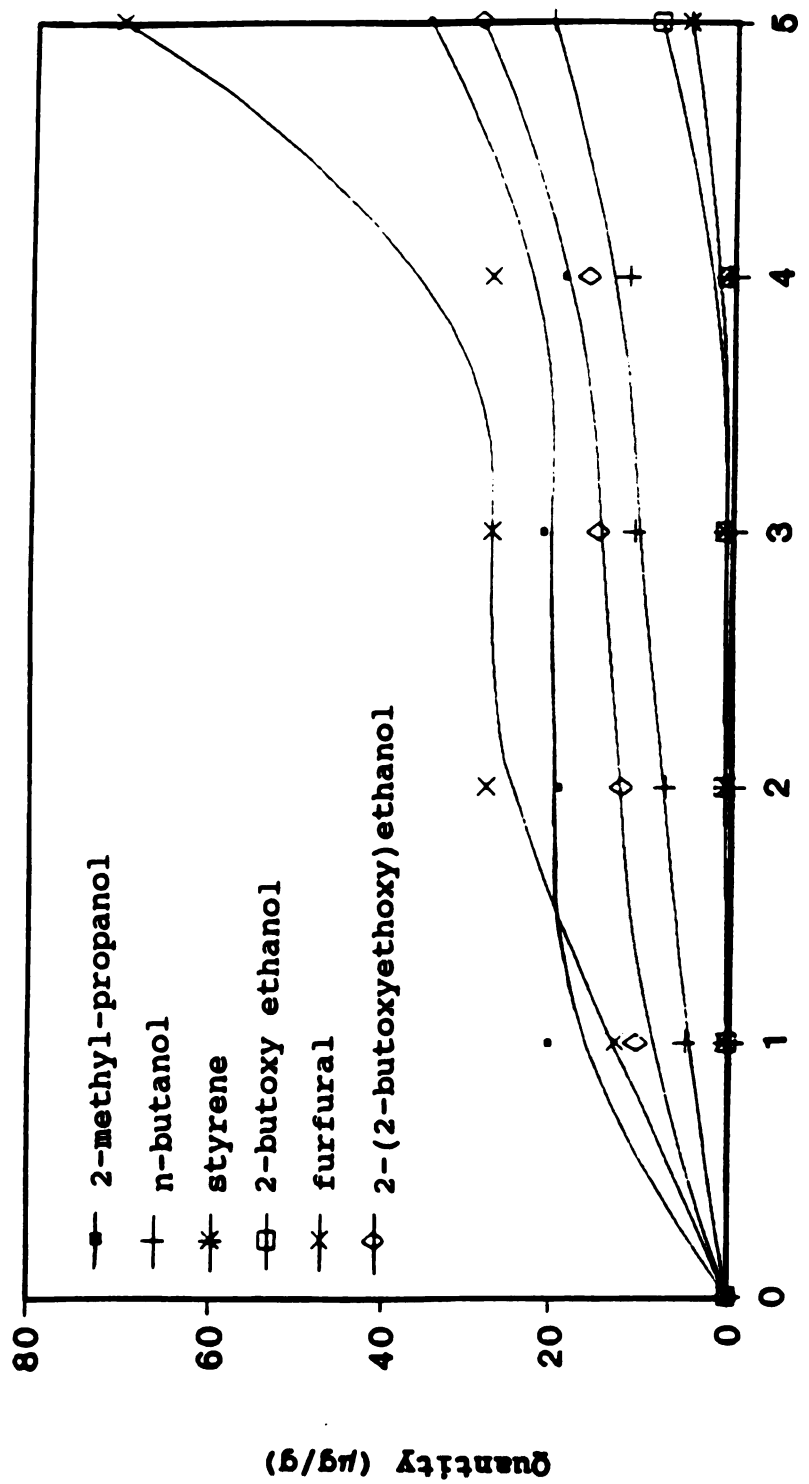

Figure 11. Quantity of volatiles released from the susceptor during heating in the microwave oven for 1 - 5 minutes, measured using the headspace technique.

5 minutes, the level of volatiles increased enormously. At the longer heating time the thermal treatment caused more degradation of the susceptor, which resulted in greater release of all probe components.

The reproducibility of replicate (n=4) assays was quite poor for these analytes, since the standard deviation was approximately 8 - 50% (Table 7). Air-dried susceptors usually contain between 0 to 12% water (wt/wt) (Booker, 1989). Thermal degradation of susceptor in a sealed vial results in the presence of condensed water. The condensed water occupies the headspace of the vial, and thus reduces the analytes in the gas phase. Also, the temperature of a specific point on a susceptor surface changes with time, as it is irradiated in a microwave (Rousselo, 1990). Because of the difficulty of obtaining or guaranteeing uniformity of radiation it is best that any analytical protocol used to evaluate microwave materials utilize conductive heating (Booker, 1989).

Booker (1989) demonstrated that microwave-interactive products degrade because of the heat generated by the susceptor element. To compare the sensitivity of the headspace and diffusion trapping methods, the susceptor was heated in an oil bath which was maintained at specific temperatures.

4.1.2 Microwave vs Conventional Heating

The same glass apparatus which was heated in a microwave oven was also immersed in an oil bath to heat the susceptor sample by conduction (Rousselo, 1990). The susceptor sample was placed in the oil bath at specific temperatures of 180, 200 and 220 ± 1°C, from 1 to 5 minutes. A comparison of the level of the six volatiles released due to microwave exposure and three oil bath temperatures at 5 minutes is presented in Figure 12. As shown, a higher level of volatiles was produced by microwave radiation in comparison to oil bath heating. Because the temperature of a specific point on a susceptor surface changes with time as it is irradiated, the release of volatiles in a temperature-dependent reaction will not be linear (Booker, 1989). Thus, the nonlinear heating process in the microwave oven results in higher temperature and more than seven times as much furfural being produced by microwave heating than in an oil bath at 200°C (Figure 12).

The quantities of volatiles released at the various oil bath temperatures are shown in Tables 8 - 10. The reproducibility of the volatiles released from the susceptor by conventional heating was only slightly better than that induced by microwave heating. The poor reproducibility is caused not only by the uneven heating in the microwave oven, but also the lack of precision associated with the headspace technique.

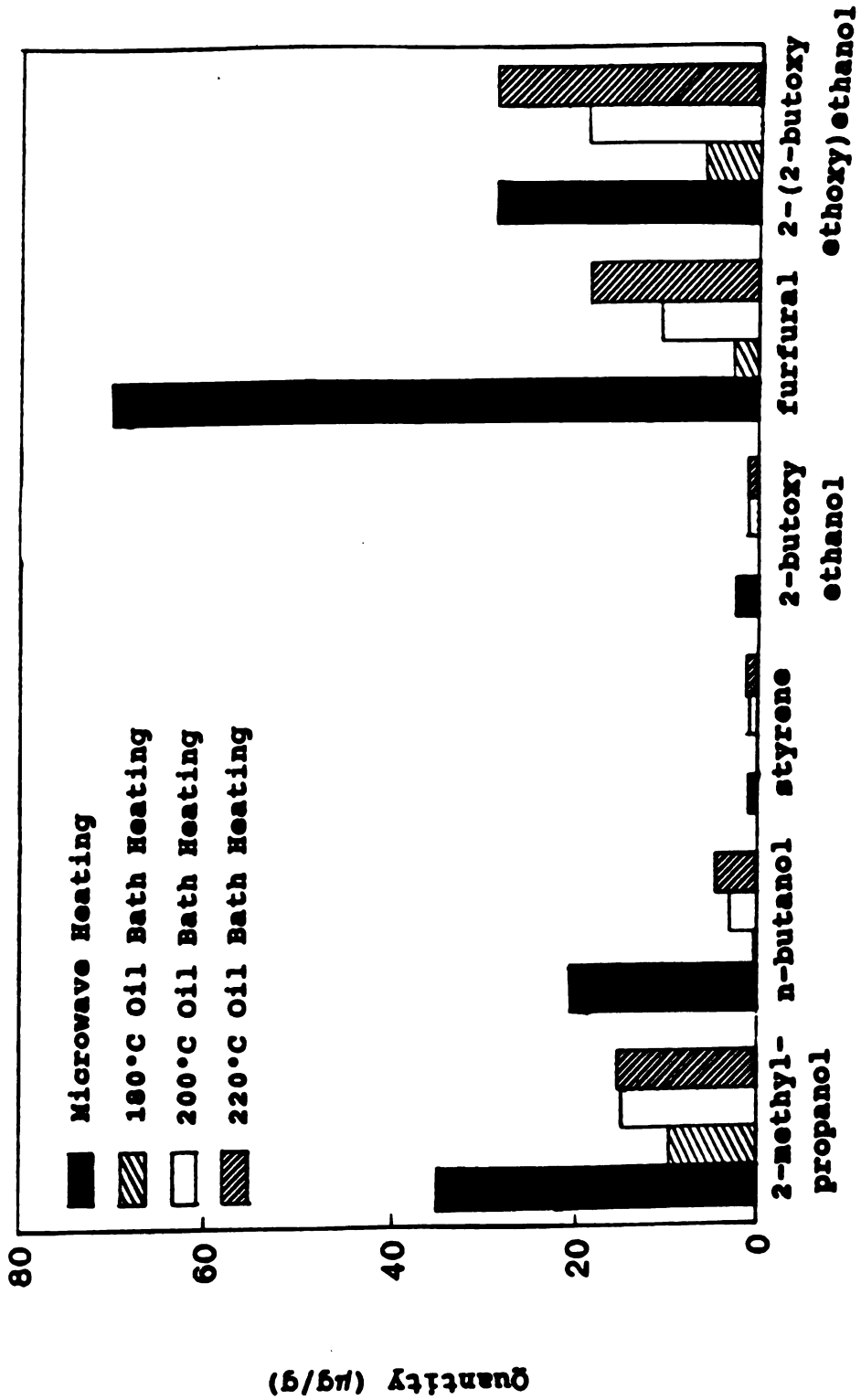

Figure 12. Quantity of volatiles released from the susceptor heated in the microwave oven and at several oil bath temperatures for 5 minutes, measured using the headspace technique.

Table 8. Volatiles released from the susceptor material during heating in an oil bath at 180°C using the headspace technique.

Time (min)	Quantity (μg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	0.46±0.18	0.18±0.00	0.00±0.00
2	3.08±0.57	0.04±0.01	0.00±0.00
3	4.57±0.63	0.05±0.01	0.00±0.00
4	7.25±0.92	0.23±0.05	0.00±0.00
5	9.66±1.50	0.50±0.06	0.00±0.00

Time (min)	Quantity (μg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.00±0.00	0.00±0.00	0.66±0.02
2	0.00±0.00	0.00±0.00	0.99±0.20
3	0.00±0.00	0.00±0.00	1.32±0.32
4	0.00±0.00	0.00±0.00	3.87±0.49
5	0.16±0.00	0.68±0.01	5.93±0.98

Table 9. Volatiles released from the susceptor material during heating in an Oil Bath at 200°C using the headspace technique.

Time (min)	Quantity (µg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	0.87±0.24	0.00±0.00	0.00±0.00
2	6.32±0.23	0.24±0.01	0.00±0.00
3	9.28±1.54	0.51±0.01	0.00±0.00
4	8.08±1.43	1.69±0.04	0.28±0.01
5	15.10±2.65	3.16±0.16	0.98±0.22

Time (min)	Quantity (µg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.00±0.00	3.82±1.15	2.31±0.05
2	0.00±0.00	5.27±1.28	6.99±1.13
3	0.00±0.00	7.75±1.64	7.53±2.66
4	0.00±0.00	8.21±0.72	8.74±2.56
5	0.00±0.00	8.83±2.11	9.15±2.89

Table 10. Volatiles released from the susceptor material during heating in an oil bath at 220°C using the headspace technique.

Time (min)	Quantity (μg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	1.67±0.10	0.00±0.00	0.00±0.00
2	7.31±1.17	0.27±0.01	0.91±0.02
3	8.74±2.64	0.59±0.23	0.94±0.05
4	14.94±0.58	2.65±0.58	1.22±0.11
5	15.57±2.64	4.52±0.25	1.38±0.25

Time (min)	Quantity (μg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.00±0.00	6.42±0.65	9.24±0.25
2	0.00±0.00	7.28±0.11	14.33±0.54
3	0.00±0.00	8.63±2.25	15.49±2.66
4	0.00±0.00	10.56±1.04	16.33±1.56
5	0.00±0.00	15.80±0.99	28.98±3.89

A comparison of the gas chromatogram of the volatiles released from the susceptor due to 1 minute microwave radiation and 4 minutes oil bath heating at 200°C is shown in Figure 13. Either heating method resulted in release of the same, major volatiles. Thus, a valid testing procedure can be designed around conventional heating as well as microwave heating.

4.2 Diffusion Trapping Technique

The six major compounds isolated from the susceptor were identified as: 2-methyl propanol, n-butanol, styrene, 2-butoxy ethanol, furfural and 2-(2-butoxyethoxy)ethanol. Identification was made by comparing retention times of the unknowns to that of the standards and by using the mass spectrometry data of Rousselo (1990). Quantification of volatile compounds was accomplished using the diffusion trapping method. The vial containing the susceptor and Tenax was heated in an oil bath at specific temperatures of 180, 200 and 220 ± 1°C from 1 to 5 minutes. After 16 hours of equilibration at 45°C, the Tenax was removed from the sorption tube and loaded into the injection port liner of the GC for analysis. The quantity of volatiles released at the various oil bath temperatures is shown in Tables 11-13. The retention time of each compound was slightly different from those determined using the static headspace technique.

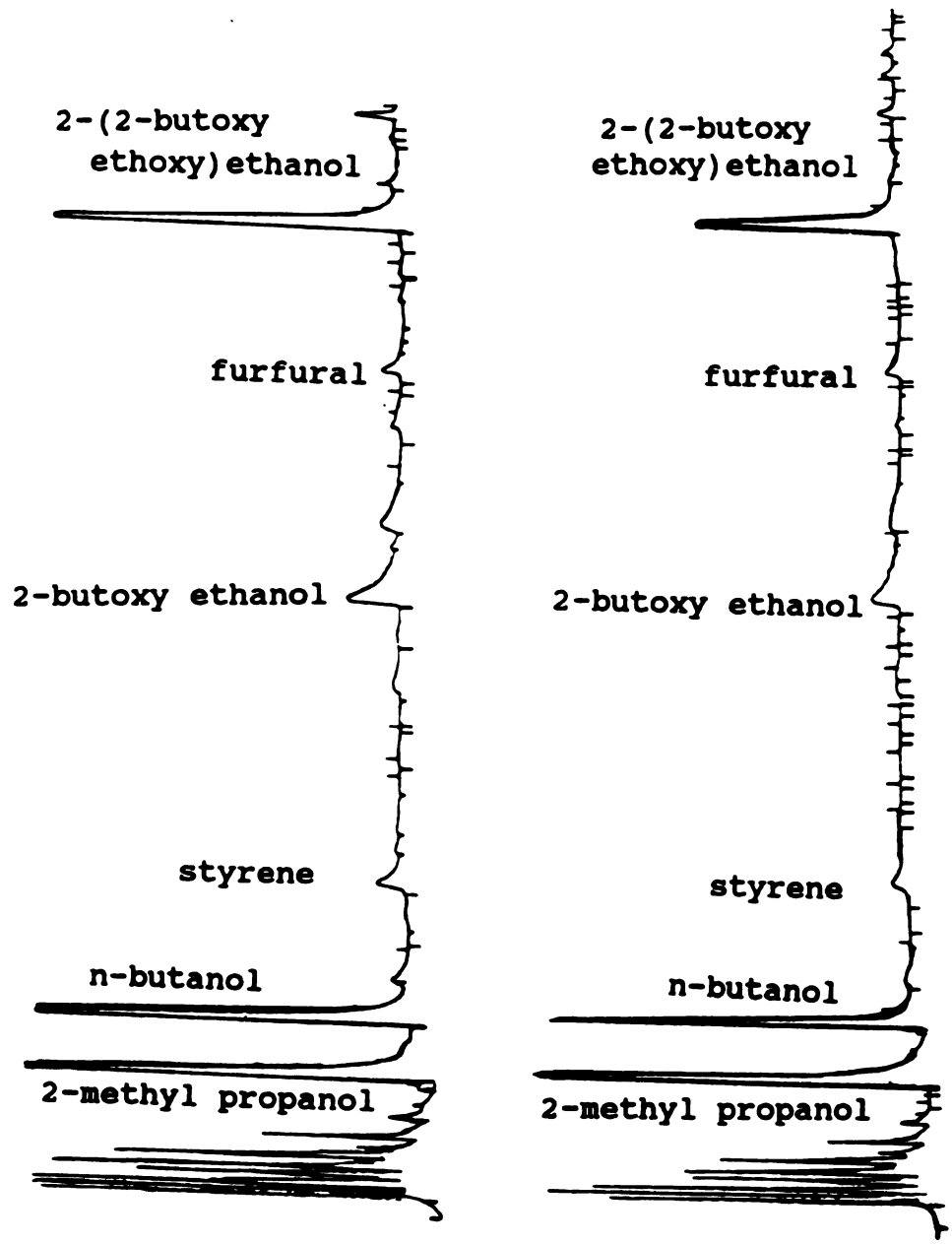

Figure 13. Top: gas chromatogram of susceptor exposed to microwave heating for 1 minute.
Bottom: gas chromatogram of susceptor heated to 200°C for 4 minutes in an oil bath.

Table 11. Volatiles released from the susceptor material during heating in an oil bath at 180°C using the diffusion trapping method.

Time (min)	Quantity (μg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	2.60±0.48	0.00±0.00	0.00±0.00
2	8.91±1.42	0.98±0.11	0.06±0.01
3	8.94±1.37	6.13±1.12	0.19±0.03
4	9.87±0.53	6.35±1.31	0.20±0.02
5	12.70±1.71	9.31±2.23	0.40±0.05

Time (min)	Quantity (μg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.09±0.01	1.05±0.13	25.09±4.38
2	1.70±0.28	2.14±0.50	31.92±3.89
3	1.75±0.17	5.42±1.12	47.72±5.34
4	1.72±0.15	6.11±1.36	48.39±1.48
5	2.25±0.60	20.61±2.65	70.58±10.56

Table 12. Volatiles released from the susceptor material during heating in an oil bath at 200°C using the diffusion trapping method.

Time (min)	Quantity (µg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	6.55±0.33	0.00±0.00	0.00±0.00
2	14.57±2.67	1.55±1.03	0.07±0.02
3	15.54±4.99	6.50±1.59	0.18±0.05
4	17.52±4.33	6.81±1.45	0.14±0.07
5	18.26±2.65	10.22±2.32	2.04±0.25

Time (min)	Quantity (µg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.11±0.01	1.35±0.16	27.97±3.78
2	2.07±0.45	2.54±0.55	50.05±3.18
3	2.18±0.27	5.98±1.80	51.75±7.83
4	2.18±0.35	5.99±1.50	53.29±3.17
5	3.73±0.98	35.08±10.2	81.18±12.1

Table 13. Volatiles released from the susceptor material during heating in an oil bath at 220°C using the diffusion trapping method.

Time (min)	Quantity (μg/g, n=4)		
	2-methyl propanol	n-butanol	styrene
1	13.58±3.60	1.51±0.33	0.02±0.00
2	16.14±1.60	8.30±1.86	0.21±0.08
3	16.60±5.24	8.77±2.51	0.83±0.30
4	18.52±2.38	10.42±4.23	1.59±0.50
5	19.89±2.77	15.27±3.53	2.62±0.98

Time (min)	Quantity (μg/g, n=4)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	1.59±0.20	0.10±0.03	54.38±17.4
2	3.84±0.98	4.33±1.28	223.00±42.2
3	4.43±0.61	21.39±6.14	254.89±40.5
4	6.18±1.95	61.16±18.9	289.06±65.1
5	11.80±2.92	74.99±18.5	414.83±60.2

For diffusion trapping, the retention times of the six compounds, 2-methyl propanol, butanol, styrene,2-butoxy ethanol, furfural and 2-(2-butoxyethoxy)ethanol were 4.72, 6.8, 12.67, 20.54, 26.17 and 43.20 minutes, respectively. Variation in retention times between the two techniques was relatively constant, which enabled the peaks to be identified. Variation in retention times between headspace and diffusion trapping may be attributed in part to the manual placement of the Tenax into the injection port of the GC in the diffusion trapping procedure.

4.2.1 Diffusion Trapping vs Headspace Technique

The headspace technique and diffusion trapping method were easily compared by heating the respective sample in an oil bath, under identical conditions. Levels of the six compounds measured using the two techniques after 5 minutes at 200°C are shown in Figure 14. Using the diffusion trapping method, the quantity of each of the analytes was higher than that found using the headspace techniquem, at the same heating temperature. As shown in Figure 14, furfural and 2-(2-butoxyethoxy)ethanol were present at higher levels by the diffusion trapping procedure. Furfural and 2-(2-butoxyethoxy)ethanol have higher boiling points and lower vapor pressures than the other four compounds. It is thus difficult to obtain the uniformity in the gas phase in a sealed vial, which results in underestimation of furfural and 2-(2-butoxyethoxy)ethanol, using the headspace method.

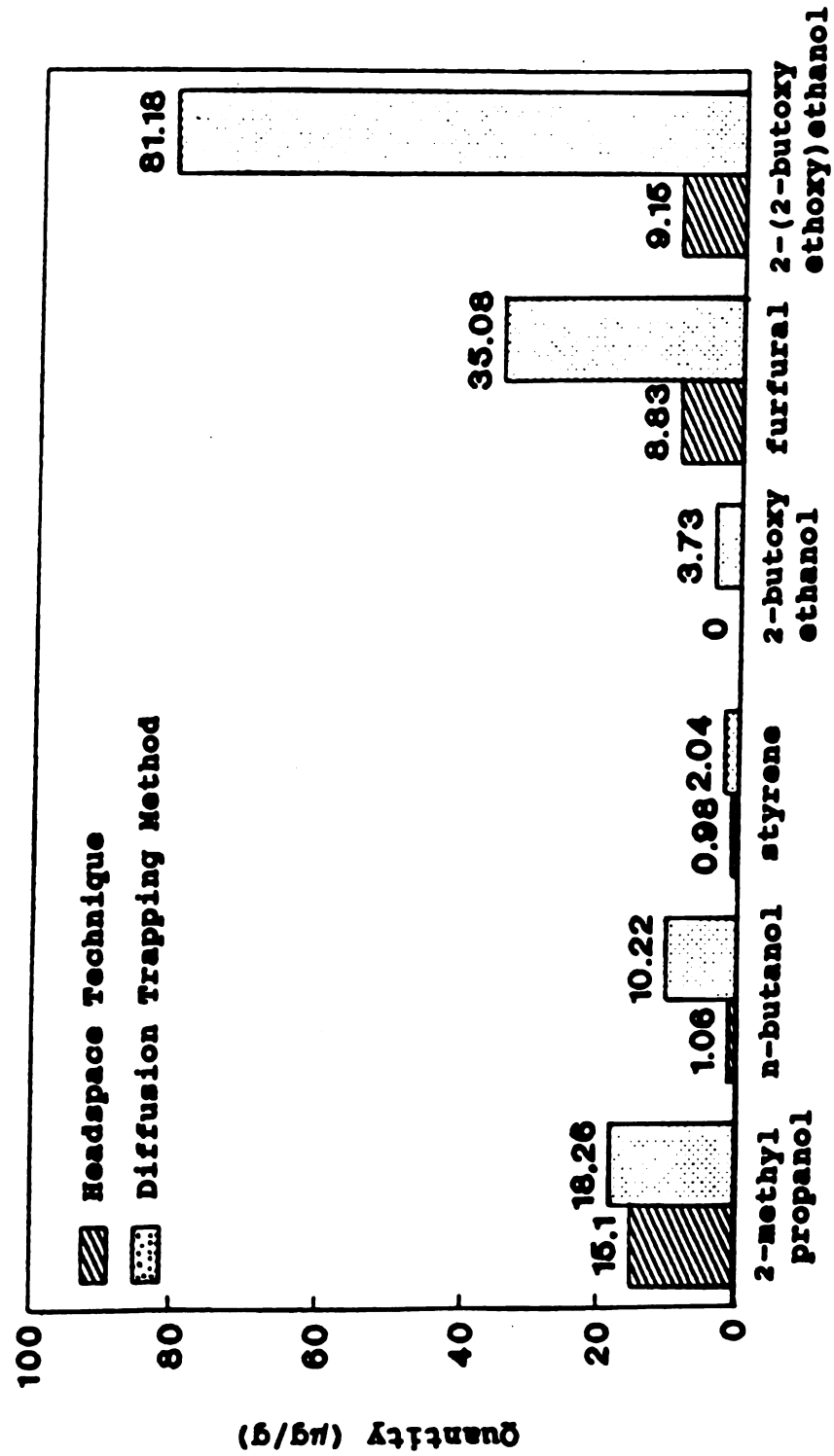

Figure 14. Quantity of volatiles released from susceptor heated in a 200°C oil bath for 5 minutes, measured using the diffusion trapping and headspace technique.

The relative difference in the quantity of furfural measured using the two techniques at three oil bath temperatures (180, 200 and 220°C) during heating for 5 minutes is shown in Figure 15. There was a difference between the two techniques at all three oil bath temperatures. Higher heating temperatures increased the relative difference in the amount of volatiles between the headspace and diffusion trapping techniques.

4.2.2 Volatile Products

As thermal degradation occurs, two groups of volatile components are released: thermal desorption compounds which are indigenous to the material (residual chemicals from the papermaking process and solvents from adhesives, etc.), and pyrolysis products from paperboard, coatings, inks, etc.

Furfural, which is generated by the decomposition of pentosans, is one of the primary pyrolysis products of paperboard (Booker, 1989). Figure 16 shows the quantity of furfural released after heating at 180, 200 and 220°C for 1 - 5 minutes. Increasing temperature and heating time resulted in a higher quantity of furfural, suggesting that furfural is produced by pyrolysis of the susceptor material. The pyrolysis volatiles appear at elevated temperatures, and are continuously generated without achieving their stoichiometric limit. Another volatile compound produced by pyrolysis is styrene. Styrene is produced by the degradation of polymers such as polystyrene or styrene

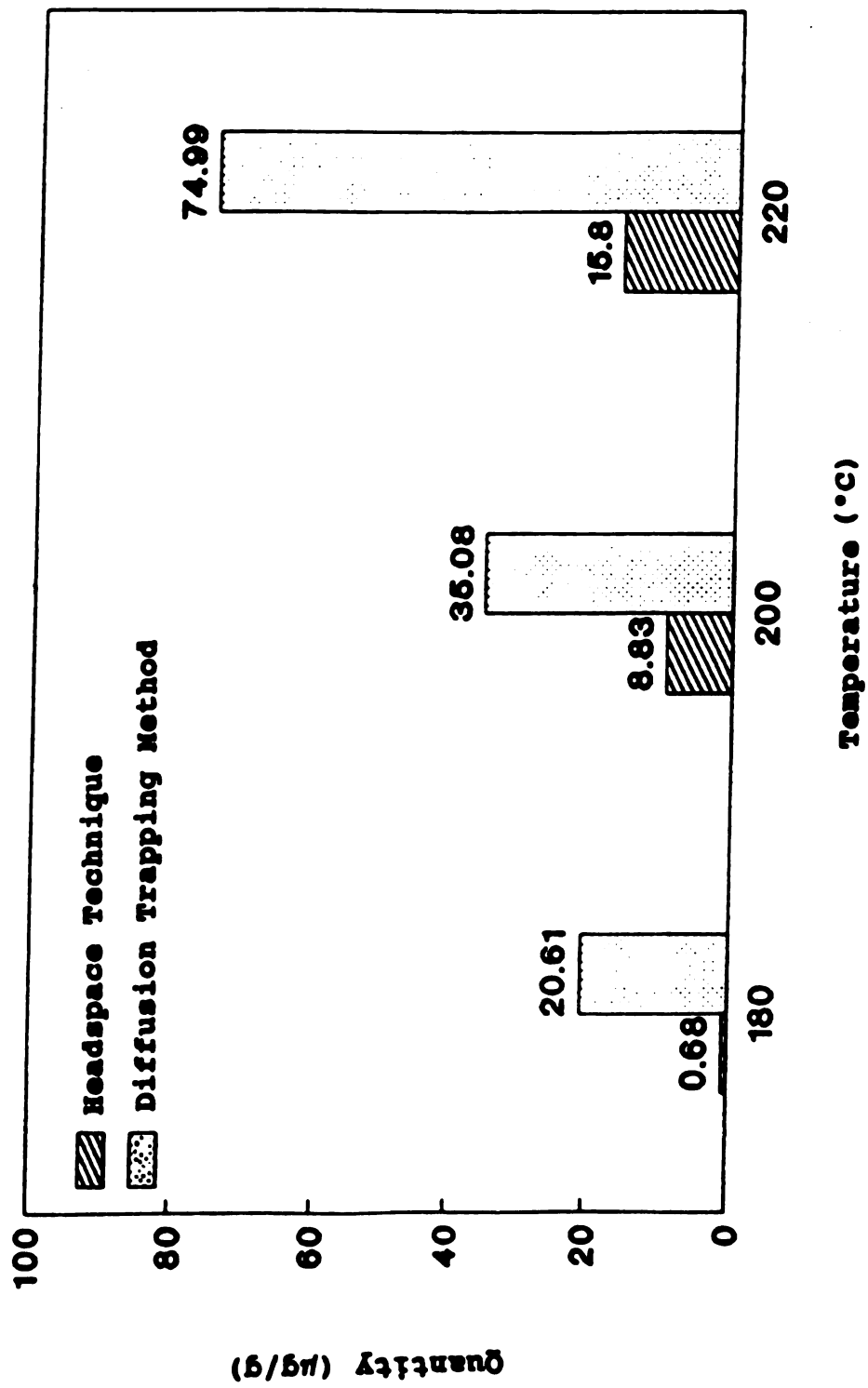

Figure 15. Quantity of furfural released from the susceptor heated in an oil bath 180, 200 and 220°C for 5 minutes, measured using the diffusion trapping and headspace techniques.

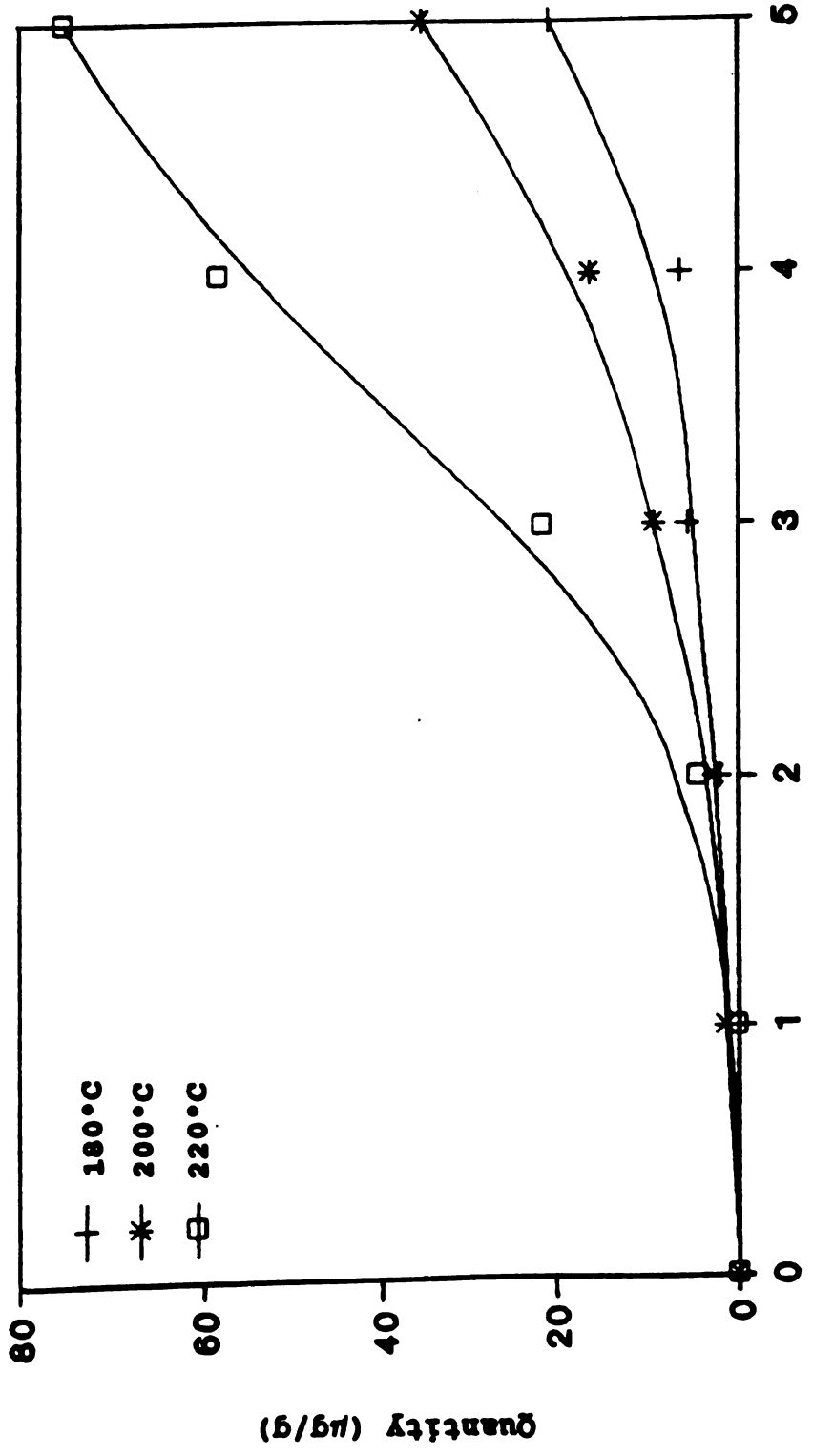

Figure 16. Quantity of furfural released from the susceptor heated in an oil bath 180, 200 and 220°C for 1 - 5 minutes, measured using the diffusion trapping method.

butadiene rubber, and will only appear at elevated temperatures (Booker, 1989). Therefore, the production of styrene (Figure 17) is similar to that found for furfural (Figure 16).

2-methyl propanol is a residual solvent from an adhesive and thus is a thermal desorption compound. Figure 18 shows the quantity of 2-methyl propanol released after heating at 180, 200 and 220°C for 1 - 5 minutes. The plots of quantity vs heating time for furfural (Figure 16) and for 2-methyl propanol (Figure 18) are distinguishably different. The 2-methyl propanol in the gas phase increased rapidly during the first 2 minutes, and did not significantly increase thereafter. The other volatiles, n-butanol, 2-butoxy ethanol and 2-(2-butoxyethoxy)ethanol, are also thermal desorption compounds. Similar desorption profiles were obtained for these compounds (Figures 19, 20 and 21). During heating these analytes increased rapidly and did not significantly increase from 2 to 4 minutes. After 5 minutes, the susceptor underwent severe degradation, and delamination and the amount of volatiles increased substantially.

4.2.3 Limitation of Diffusion Trapping Method

The diffusion trapping technique is more sensitive than the headspace technique under the same heat treatment. However, there are two problems which limit its utility.

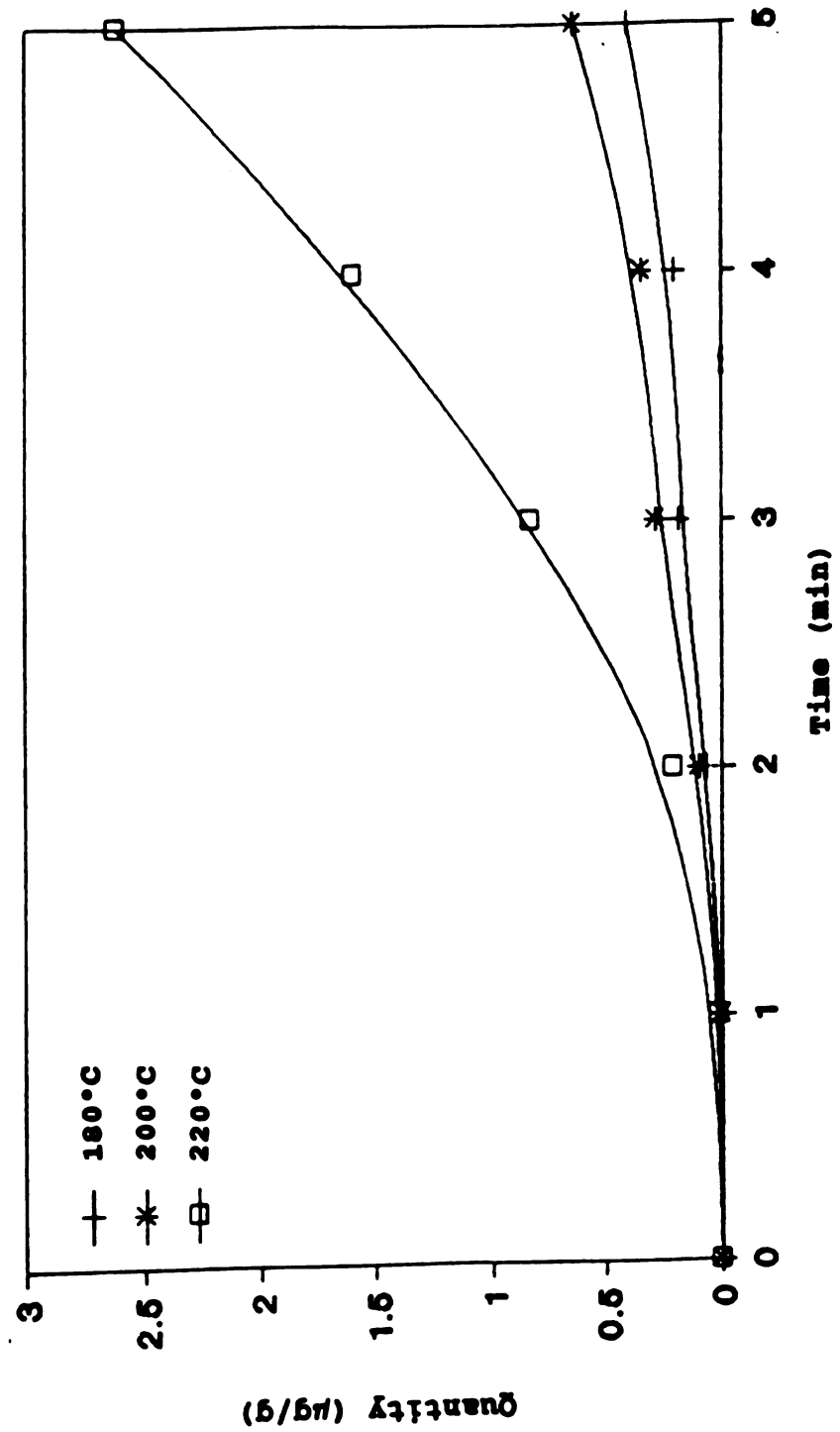

Figure 17. Quantity of styrene released from the susceptor heated in an oil bath 180, 200 and 220°C for 1 - 5 minutes, measured using the diffusion trapping method.

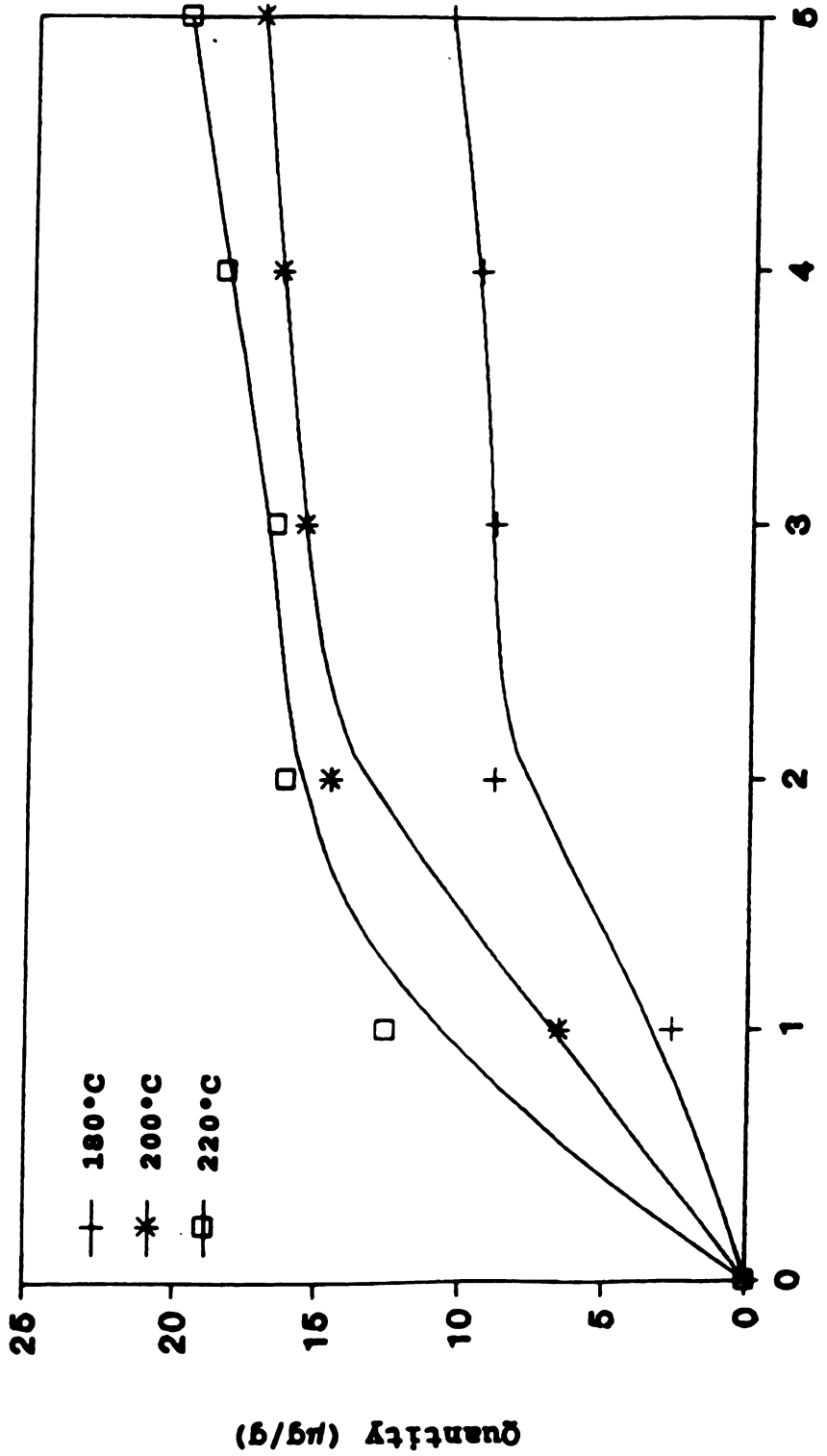

Figure 18. Quantity of 2-methyl-propanol released from the susceptor heated in an oil bath 180, 200 and 220°C for 1-5 minutes, measured using the diffusion trapping method.

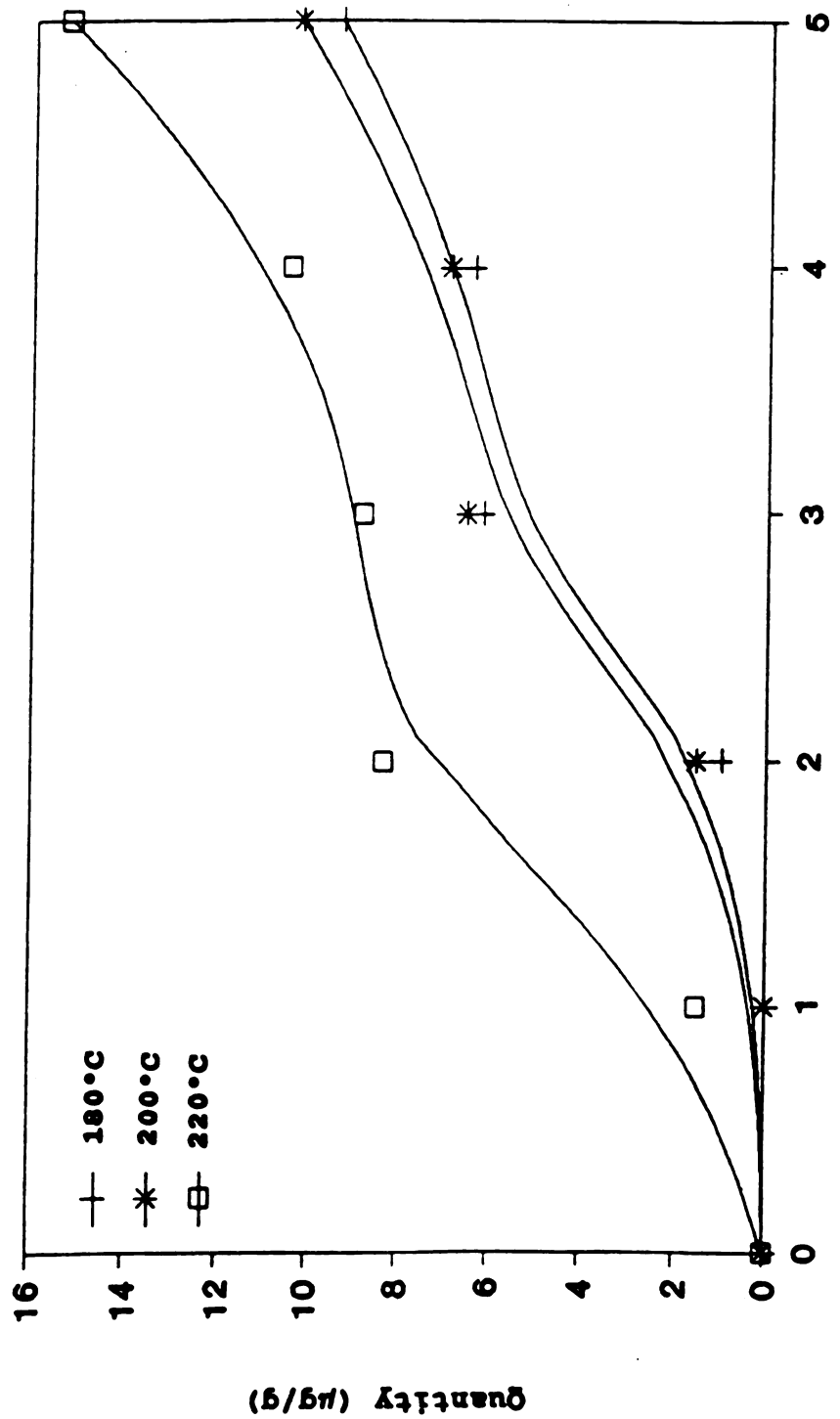

Figure 19. Quantity of n-butanol released from the susceptor heated in an oil bath 180, 200 and 220°C for 1 - 5 minutes, measured using the diffusion trapping method.

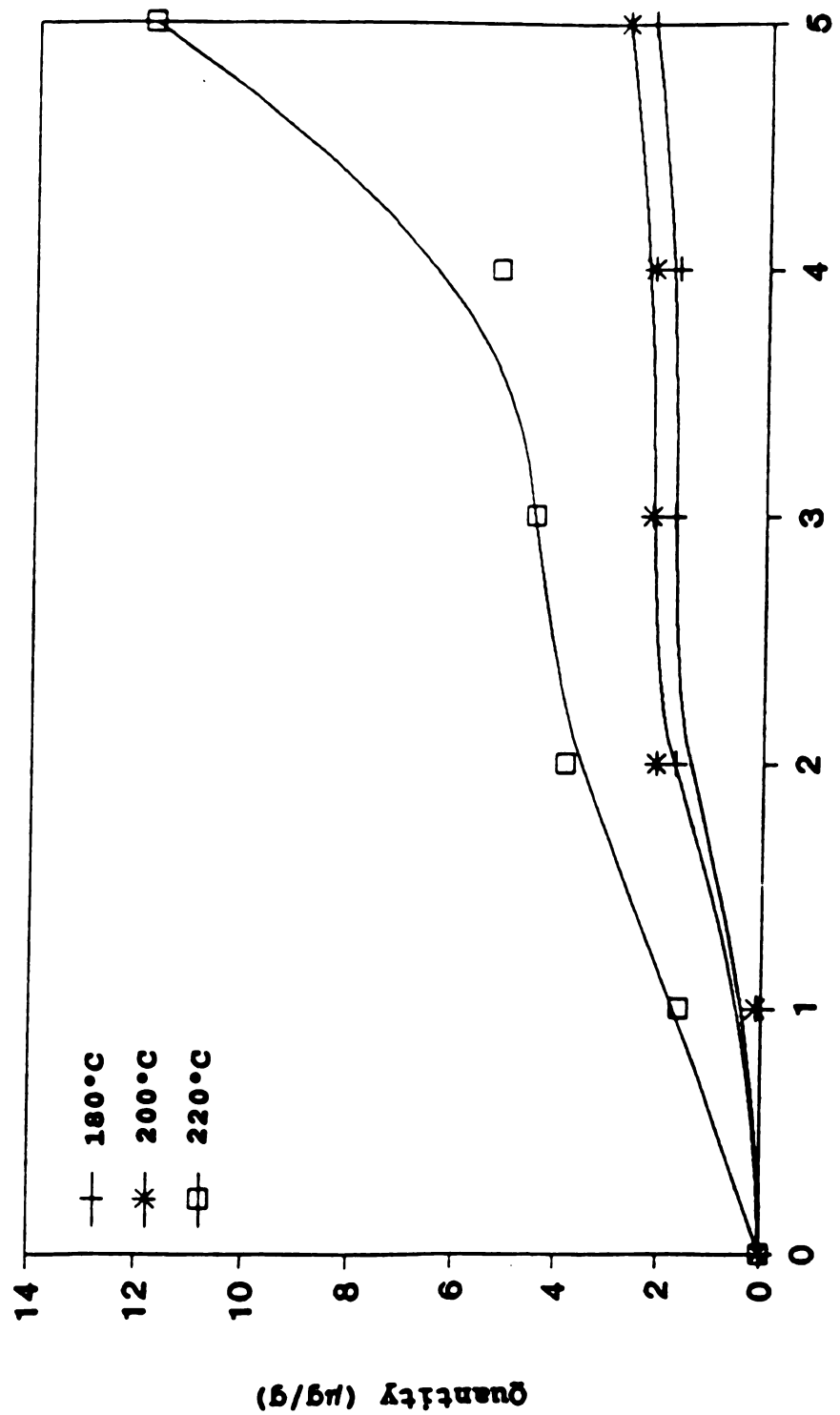

Figure 20. Quantity of 2-butoxy ethanol released from susceptor heated in an oil bath 180, 200 and 220°C for 1 - 5 minutes, measured using the diffusion trapping method.

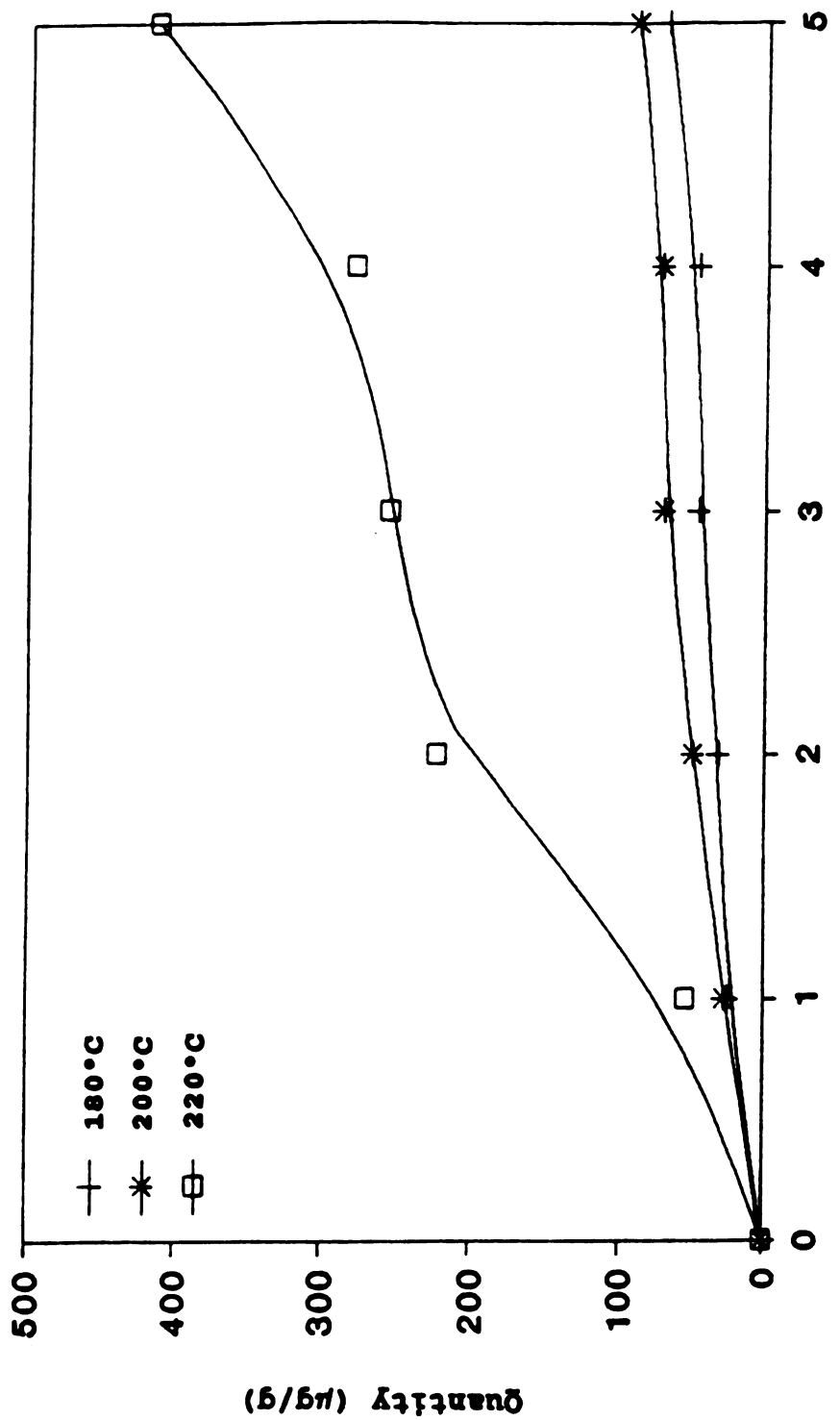

Figure 21. Quantity of 2-(2-butoxyethoxy)ethanol released from the susceptor heated at 180, 200 and 220°C for 1-5 minutes, measured using diffusion trapping technique.

First, it is more time consuming because of the time required to assure complete adsorption of the volatiles by the Tenax. Secondly, the capacity of Tenax (around 0.03 g) may be insufficient to absorb all the volatiles, which are released from a susceptor heated at high temperatures or long heating times. Since the 0 - 36% of standard deviation is large at high temperature of 220°C (Table 13), at these conditions, the Tenax may not have the capacity needed to totally sorb the volatiles produced.

4.3 Thermal Desorption Technique

The thermal desorption technique can compensate for the limitations of the diffusion trapping technique, and is a less cumbersome and quicker method while still maintaining the high sensitivity.

The thermal desorption procedure consists of two parts, a thermal stripper for volatile absorption, and a thermal desorption unit for volatile desorption into the GC. In the thermal stripper, the susceptor is placed inside the sparge vial, the sparge vial placed into the oven of the thermal stripper, and connected to a sorbent tube. The oven is then heated to a specific temperature (180 or 190°C), and the carrier gas continuously purges the liberated volatiles to the sorbent tube. Therefore, the equilibration time is practically eliminated. The sorbent tube contains around 4 g of the Carbotrap sorbent material, and thus has more

capacity than the Tenax trap (0.03 ± 0.005 g) used in the diffusion trapping procedure. Moreover, the Carbotrap material is composed of different absorbent materials, which can absorb different molecular weight volatiles, and this may reduce losses during the sorption step. In the desorption step, the sorbent tube is placed directly into the thermal desorption unit to desorb the compounds onto the GC column. The quantities of volatiles released at 180 and 190°C is shown in Tables 14 and 15. And the chromatogram of volatiles released at 180 and 190°C for 5 minutes is present in Figure 22.

Six major analytes detected from the susceptor were quantified and the retention times are as follows: 2-methyl propanol (7.10 min.), n-butanol (9.13 min.), styrene (11.87 min.), 2-butoxy ethanol (20.47 min.), furfural (25.96 min.) and 2-(2-butoxyethoxy)ethanol (41.67 min.). The retention times of the components were slightly different than those determined using the diffusion trapping technique. This problem was eliminated by injecting the headspace of these six standard compounds into the side port of the thermal stripper, and repeating the procedure used in heating the susceptor to obtain the retention times for each volatile. Comparing the retention time of the susceptor volatiles with the standards, the peaks were identified. The difference in retention times between the diffusion trapping and thermal desorption methods may be ascribed to the introduction of

Table 14. Volatiles released from the susceptor material at temperature of 180°C using the thermal desorption method.

Time (min)	Quantity (μg/g, n=3)		
	2-methyl propanol	n-butanol	styrene
1	17.44±1.41	1.04±0.01	0.21±0.03
2	34.66±0.98	2.08±0.11	0.43±0.04
3	53.17±0.43	3.05±0.06	0.79±0.05
4	61.58±2.36	4.42±0.59	1.07±0.04
5	70.22±3.29	5.15±0.51	1.45±0.04

Time (min)	Quantity (μg/g, n=3)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.20±0.01	1.01±0.11	70.56±2.16
2	0.38±0.04	1.05±0.11	104.19±7.88
3	0.48±0.02	1.08±0.02	125.11±9.62
4	0.52±0.06	1.20±0.09	129.10±5.29
5	0.97±0.08	1.37±0.15	149.40±8.05

Table 15. Volatiles released from the susceptor material at temperature of 190°C using the thermal desorption method.

Time (min)	Quantity (μg/g, n=2)		
	2-methyl propanol	n-butanol	styrene
1	59.34±3.33	3.45±0.18	0.29±0.03
2	65.44±1.15	4.15±0.01	0.60±0.05
3	77.82±7.75	5.91±0.26	0.86±0.01
4	89.86±3.54	9.57±0.12	1.14±0.07
5	91.01±1.78	10.43±0.58	1.46±0.08

Time (min)	Quantity (μg/g, n=2)		
	2-butoxy ethanol	furfural	2-(2-butoxy ethoxy)ethanol
1	0.32±0.03	1.05±0.10	94.27±8.67
2	0.48±0.04	1.05±0.09	129.38±9.48
3	0.62±0.04	1.12±0.11	138.59±6.64
4	0.67±0.01	1.23±0.07	145.21±0.86
5	1.15±0.02	1.34±0.09	164.52±1.58

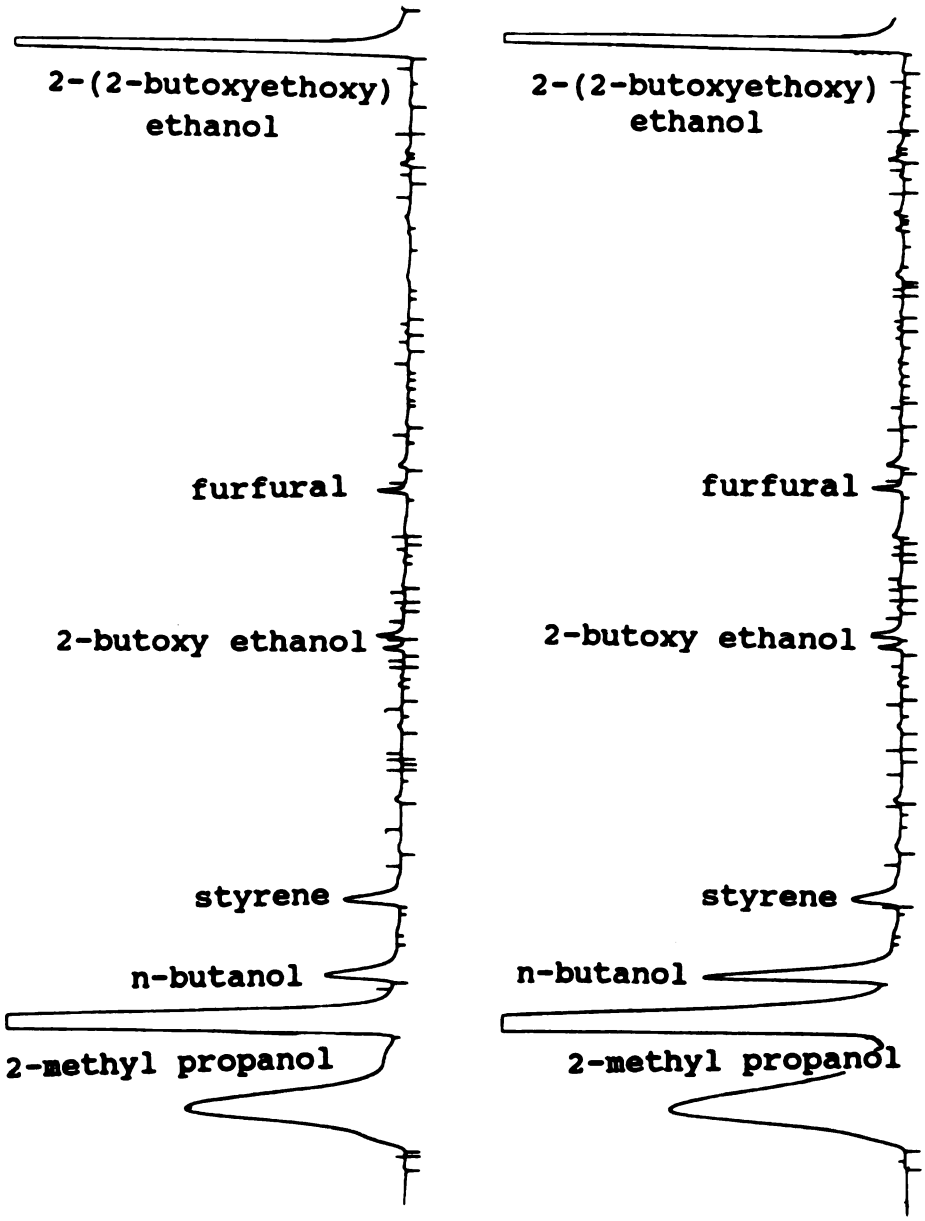

Figure 22. Top: gas chromatogram of susceptor heated to 180°C for 5 minutes in the thermal stripper
Bottom: gas chromatogram of susceptor heated to 190°C for 5 minutes in the thermal stripper

analyze compounds to the GC through a transfer line in the thermal desorption procedure.

4.3.1 Volatile Products Using the Thermal Desorption Method

The relationship between heating time and the average quantities (μg/g) of volatiles released from the susceptor during heating in the thermal desorption technique is shown in Figures 23 - 25. For the pyrolysis volatiles (styrene and furfural), the quantity of styrene increased linearly with heating time (Figure 23). For furfural, the amount did not change with increasing heating time (Figure 24). This is attributed due to the oven temperature of the thermal stripper not being high enough to thermally degrade the paperboard to produce the furfural. The oven temperature of the thermal stripper is limited to below 200°C. The effect on furfural formation can not be seen at this temperature because the pyrolysis volatiles appeared at elevated temperature levels (Booker, 1989). For thermally desorbed compounds, such as n-butanol (Figure 25), the quantity was increased as temperature and heating time increased.

Raising the oven temperature from 180 to 190°C did not effect the amount of styrene and furfural released (Figure 26). However, for the thermal desorption compounds (2-methyl propanol, n-butanol, 2-butoxy ethanol and 2-(2-butoxyethoxy)ethanol), the temperature increase from 180°C to 190°C resulted an increase in the amount of volatiles.

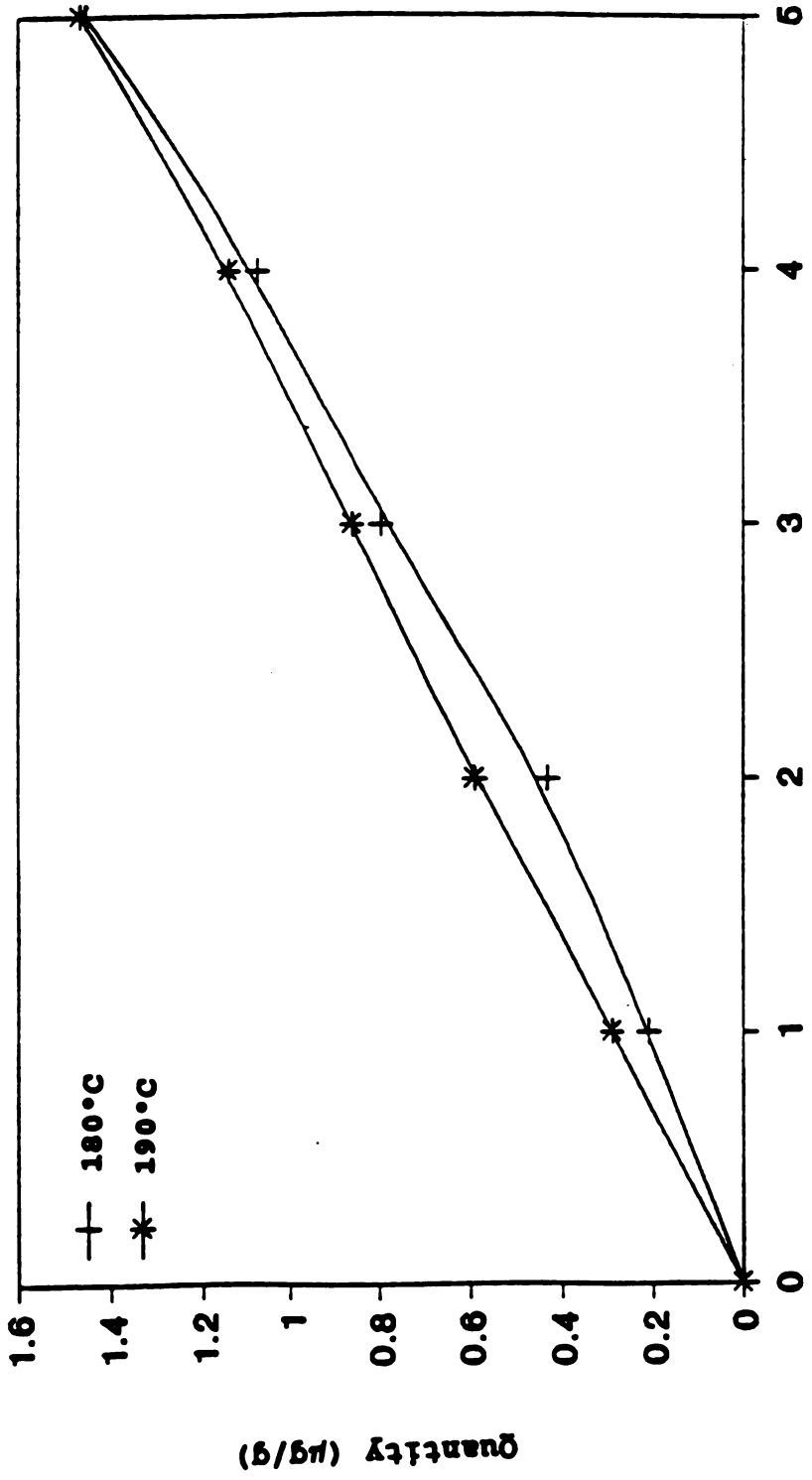

Figure 23. Quantity of styrene released from the susceptor heated at 180 and 190°C for 1 - 5 minutes, measured using the thermal desorption technique.

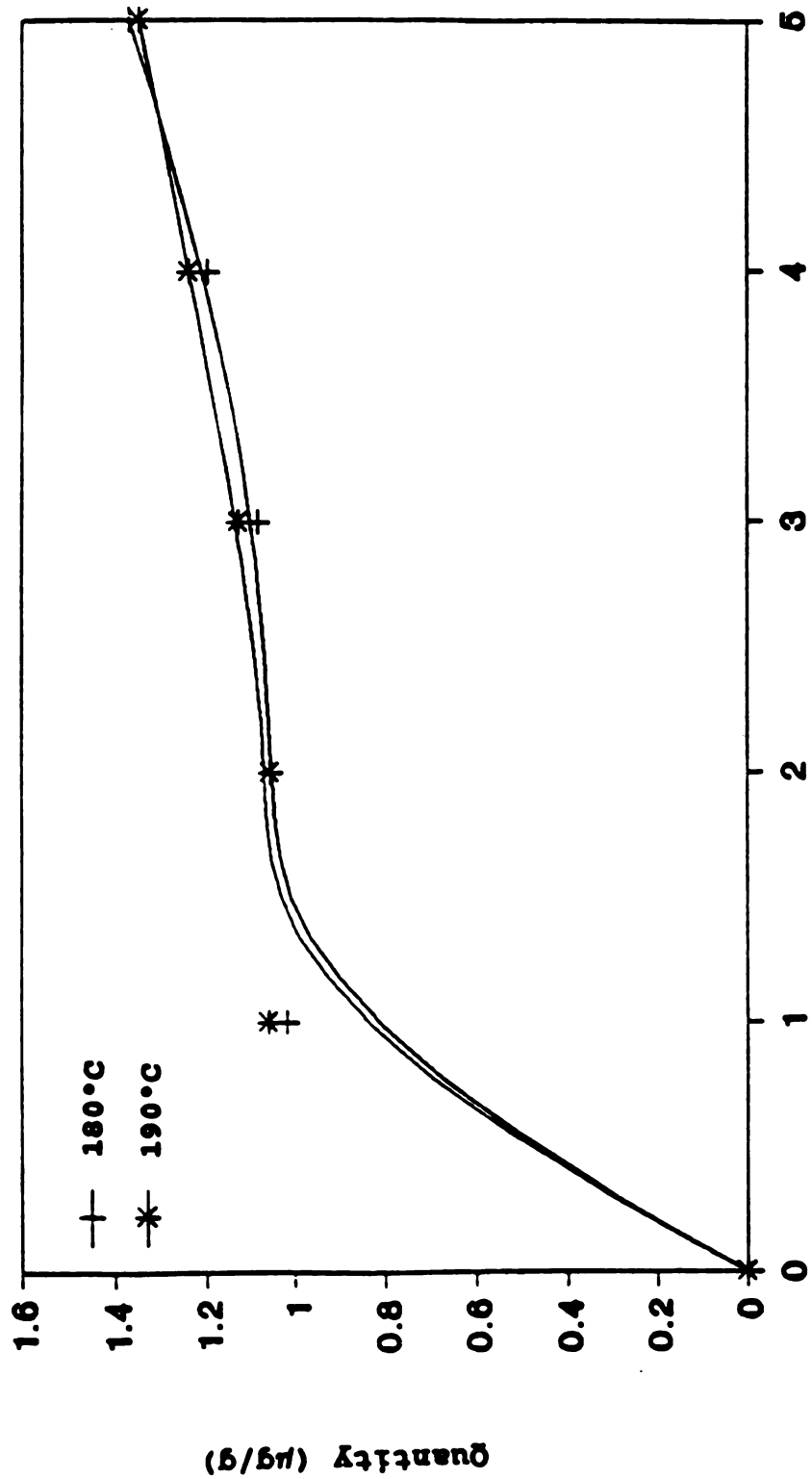

Figure 24. Quantity of furfural released from the susceptor heated at 180 and 190°C for 1 - 5 minutes, measured using the thermal desorption technique.

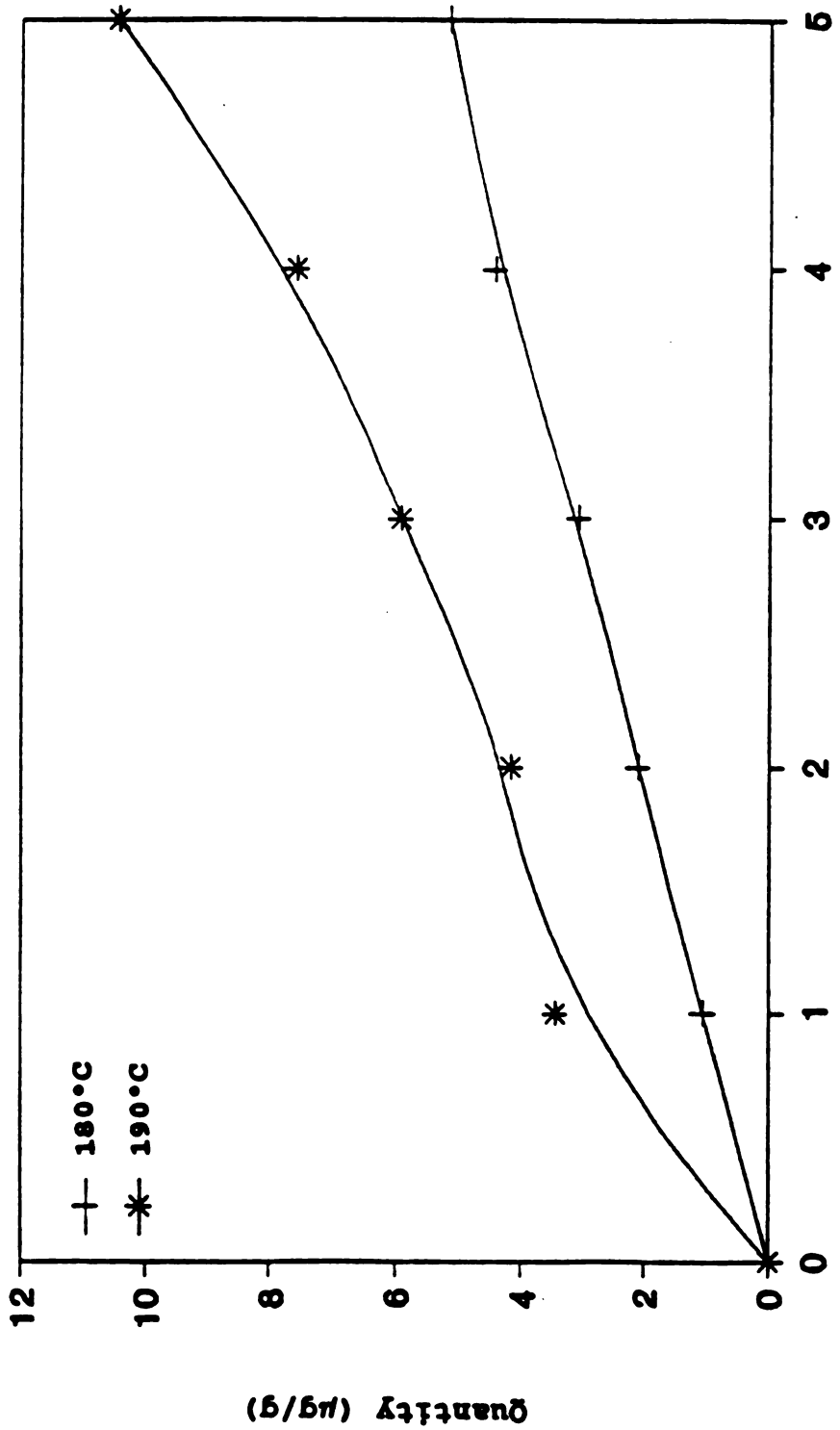

Figure 25. Quantity of n-butanol released from the susceptor heated at 180 and 190°C for 1 - 5 minutes, measured using the thermal desorption technique.

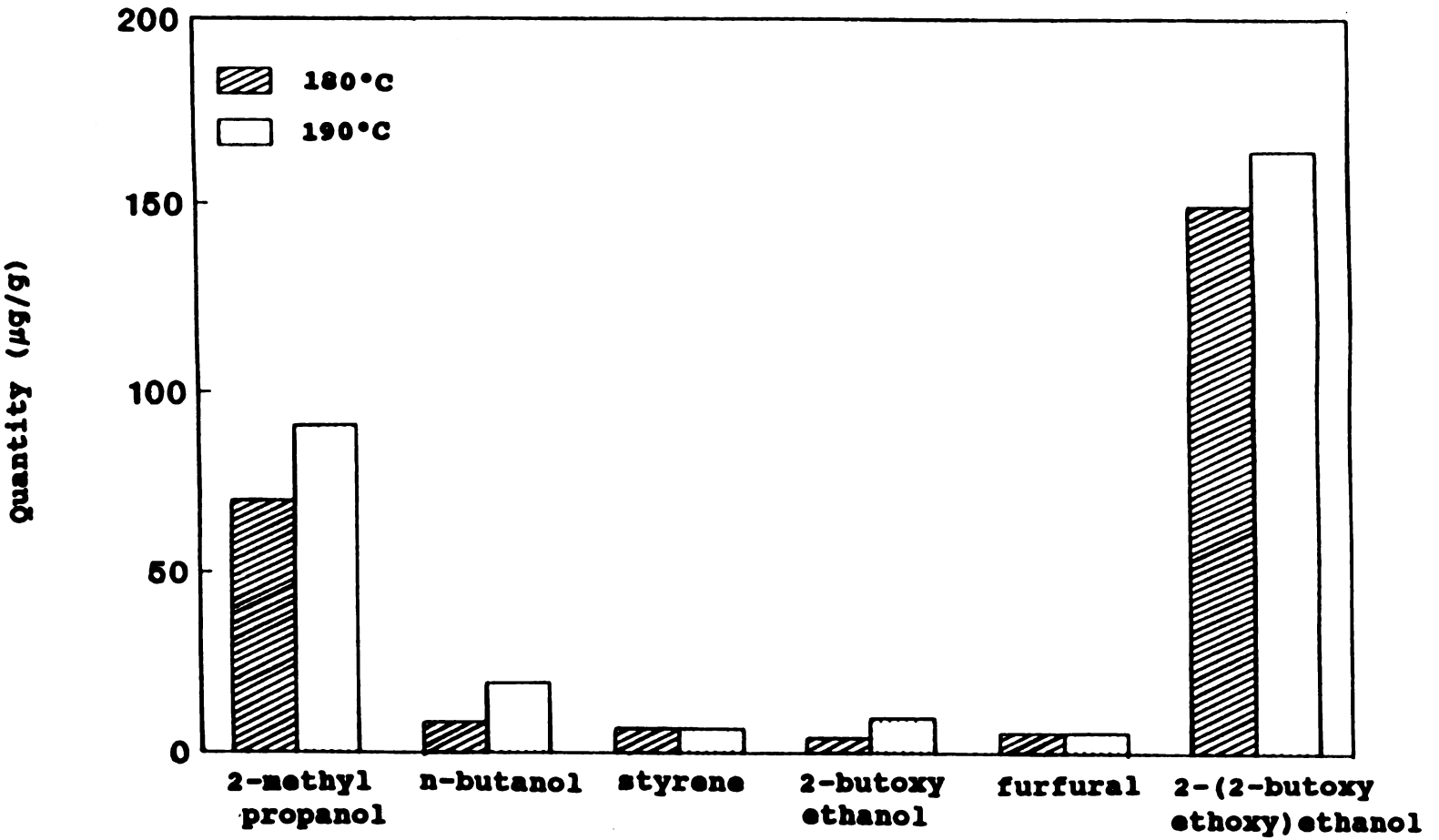

Figure 26. Quantity of volatiles released from the susceptor heated at 180 and 190°C for 5 minutes, measured using the thermal desorption technique.

4.3.2 Sensitivity of Thermal Desorption Technique

The sensitivity of an analytical method is important in determining the degradation products of a susceptor. The volatile components were measured with standard deviations of approximately 6% (Table 14) in the thermal desorption methods, in comparison to the standard deviations of 14% in the diffusion trapping method (Table 11) and 20% in the headspace technique (Table 8). The reproducibility of the thermal desorption assays is, therefore, quite good for these volatiles.

The level of the six major volatiles released from susceptor measured using the three methods, namely, headspace, diffusion trapping and thermal desorption methods, is shown in Figure 27 for studies carried out at 180°C and a 5 minutes heating time. The quantity of each volatile, as measured by the thermal desorption method was higher than by the diffusion trapping and headspace technique. Thus, the thermal desorption procedure appears to be more sensitive than the other two techniques.

A comparison of the volatiles from the susceptor after 2 minutes in an oil bath at 220°C and 5 minutes in the thermal stripper at 190°C is shown in Figure 28. Two-methyl propanol was present at higher level using the thermal desorption method, 2-(2-butoxyethoxy)ethanol was higher amount using the diffusion trapping technique. For the other volatiles, n-butanol, styrene, 2-butoxy ethanol and

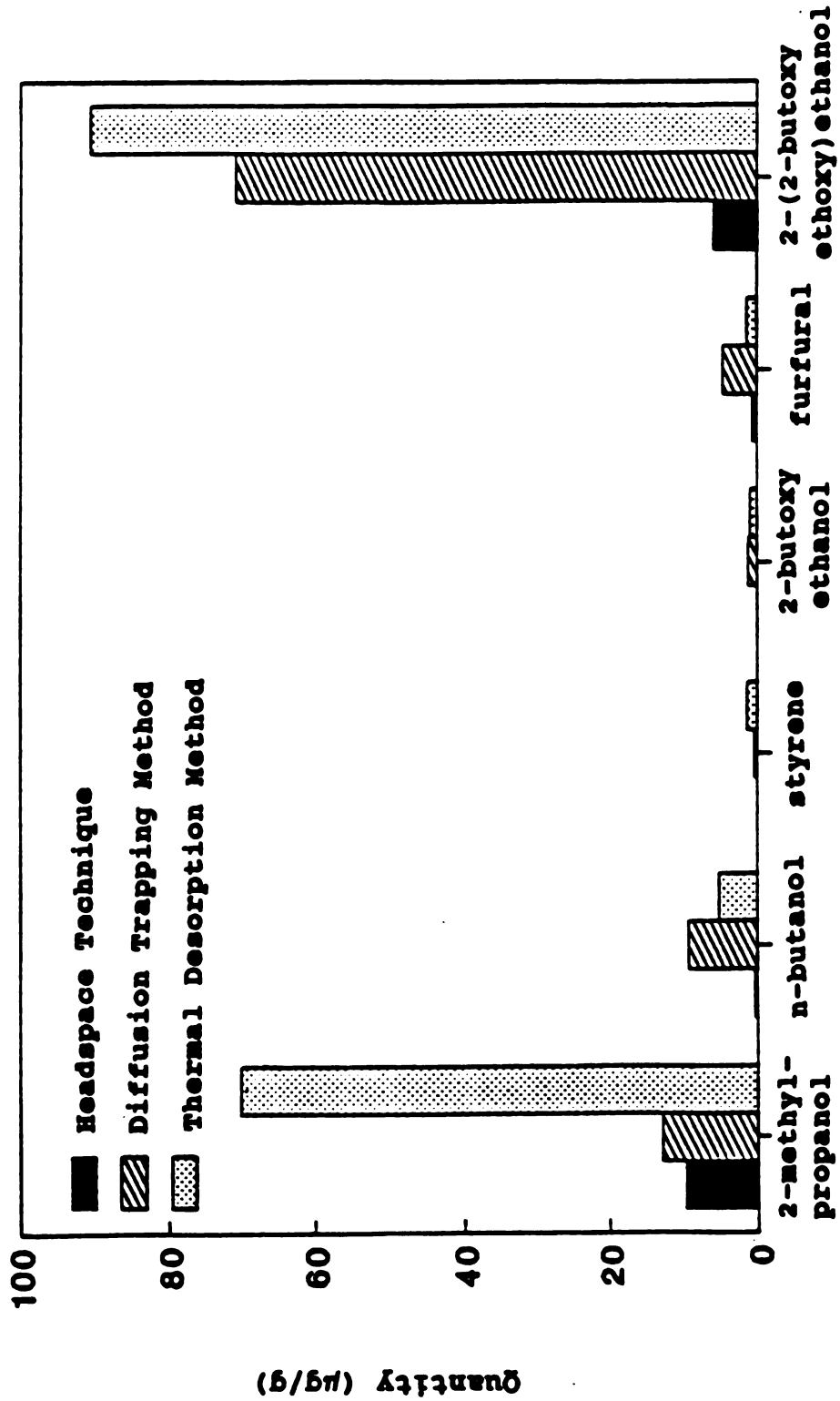

Figure 27. Quantity of volatiles released from the susceptor heating at 180°C for 5 minutes, measured using the diffusion trapping, headspace and thermal desorption methods.

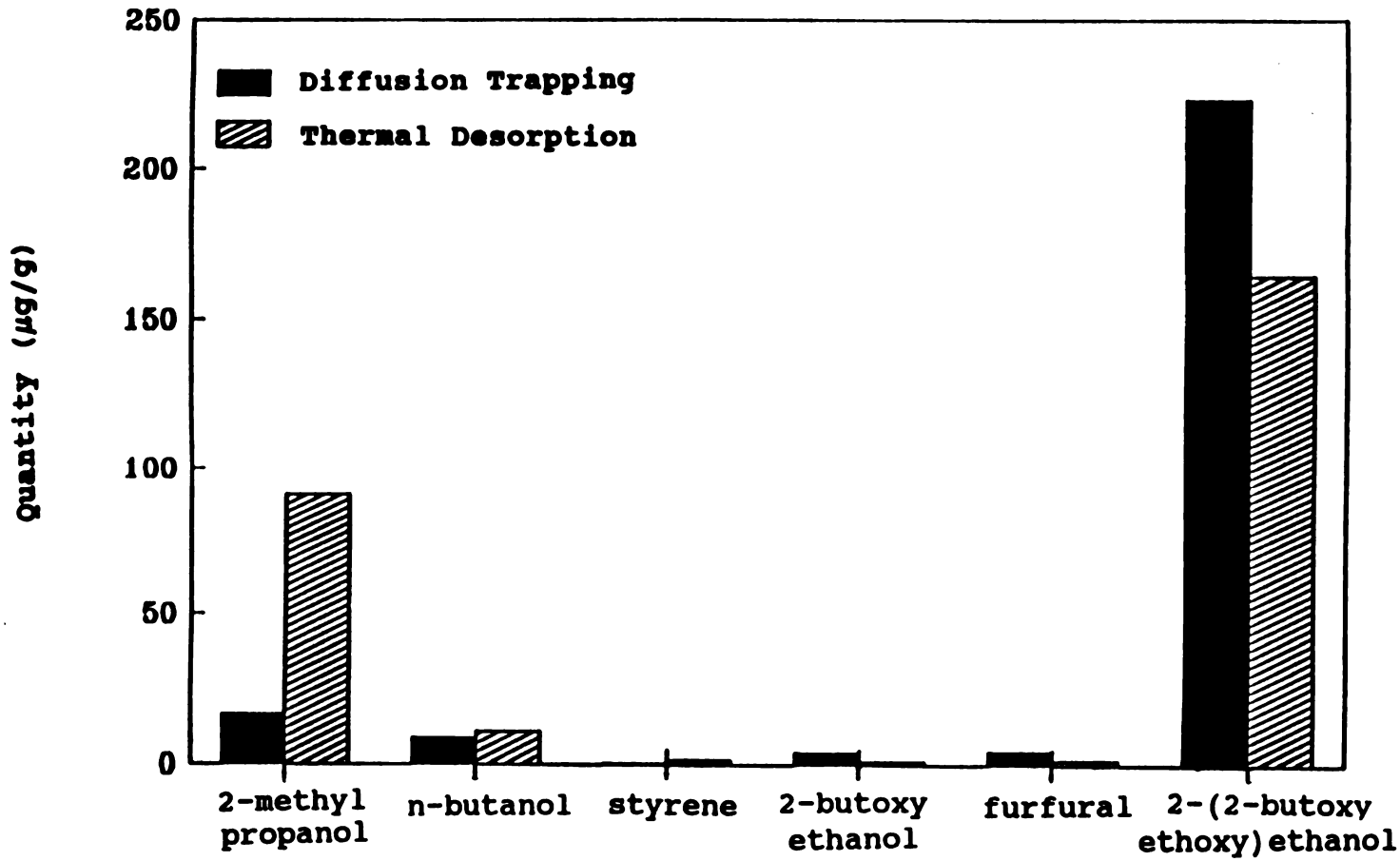

Figure 28. Quantity of volatiles released from susceptor heated in a 220°C oil bath for 2 minutes using the diffusion trapping method, and in 190°C thermal stripper for 5 minutes using the thermal desorption technique

furfural, there were similar quantities found using either of the two techniques. Thus, it is likely that a testing procedure can be developed using the thermal desorption method, which can be used to determine released of volatiles. However, it is necessary to determine what the relationship in the heating temperature and time is between the diffusion trapping and thermal desorption method.

Chapter 5

CONCLUSION

Three methods (headspace, diffusion trapping and thermal desorption techniques) were used to measure the volatiles released from a susceptor material during heating. The headspace technique is commonly used for measuring volatiles because it is simple and less time consuming than the diffusion trapping method. Also, the susceptor can be heated directly in the microwave oven. However, the microwave oven has non-uniform heating patterns which results in variability within and between ovens. Also, the size of the susceptor sample effects the temperature of the susceptor during heating in a microwave oven. Other factors such as environmental temperature, pressure, sample matrix or injection volume may also effect headspace measurement. These variations can lead to poor reproducibility within and between laboratories.

The diffusion trapping method is more sensitive than the headspace technique at the same heat treatment. Because samples prepared for diffusion trapping were heated in an oil bath, release of volatiles were less variable than for the susceptor heated in a microwave oven. However, a major disadvantage of this method is that the turnaround time for

samples is longer, due to the need to prepare samples a day in advance to allow for equilibration. The capacity of Tenax to absorb volatiles is also limited in this system, which may result in loss of volatiles and reduce the reproducibility of the method.

The thermal desorption method provides for maximum sensitivity since all of the absorbed volatiles are desorbed onto the gas chromatographic column. Moreover, the sorbent tube contains a multi-bed material which can separate the different molecular weight volatiles during the trapping procedure. Therefore, the thermal desorption method provides more sensitivity than the diffusion trapping and headspace techniques. At an oven temperature of 180°C, the thermal desorption method had excellent reproducibility. Standard deviations were below 6% for three replications. Moreover, the carrier gas continuously purges volatiles to the sorbent tube which eliminates the need to equilibrate samples. The thermal desorption technique provides for easy and rapid analysis of volatiles released from a solid sample. This technique involves heating the sample, purging using a carrier gas of the volatiles from the sample to the Carbotrap tube to the GC for analysis. This process takes about 1 hour. In addition, the thermal desorption technique can be employed for various aqueous samples using a steam distillation/thermal stripping procedure.

One of the problem which limits its current utility is the oven temperature capacity of the thermal stripper. The oven temperature can not operate in excess of 200°C. Samples were heated in the thermal stripper at 180 and 190°C, respectively. For the pyrolysis volatiles (styrene and furfural), which begin to appear at elevated temperature (220°C), quantities released at 180 and 190°C were similar. This method can not be used to predict the amount of pyrolysis products from the susceptor because the temperature of the susceptor in microwave oven will often be greater than 200°C. The pyrolysis products appear in significant quantities above 220°C. For the thermally desorbed compounds (2-methyl propanol, n-butanol, 2-butoxy ethanol and 2-(2-butoxyethoxy)ethanol), the amount of volatiles increases enormously at higher temperatures and extended heating times. Most microwavable food cooked in contact with susceptor material is heated between 177 and 260°C. To quantify the volatiles from a susceptor in an actual food system, this oven limit must be increased. The thermal desorption technique proves to be a simple and efficient method of sample handling and measurement for volatiles.

In quantification of volatiles, a standard solution provides for more precision and reproducibility in constructing the standard curve in comparison to a headspace technique. A problem associated with the thermal desorption

method is the solvent used in the preparation of a standard solution. The solvent will overload the sorbent tube, and thus, reduce its absorbing capacity.

Further work in this area should be done to identify the origin of volatiles. Mass spectrometry and thermal desorption method can be used together to analyze individual components of susceptor material, including the paperboard, adhesive and metallized polyester layers. Another study needs to be done to establish correlation between conventional, microwave and the thermal desorption methods based on heat input. Furthermore, it will be necessary to establish standard conditions for the thermal desorption technique to quantify volatiles from susceptor materials, particularly, if the material must meet some regulatory standards.

APPENDICES

Appendix A

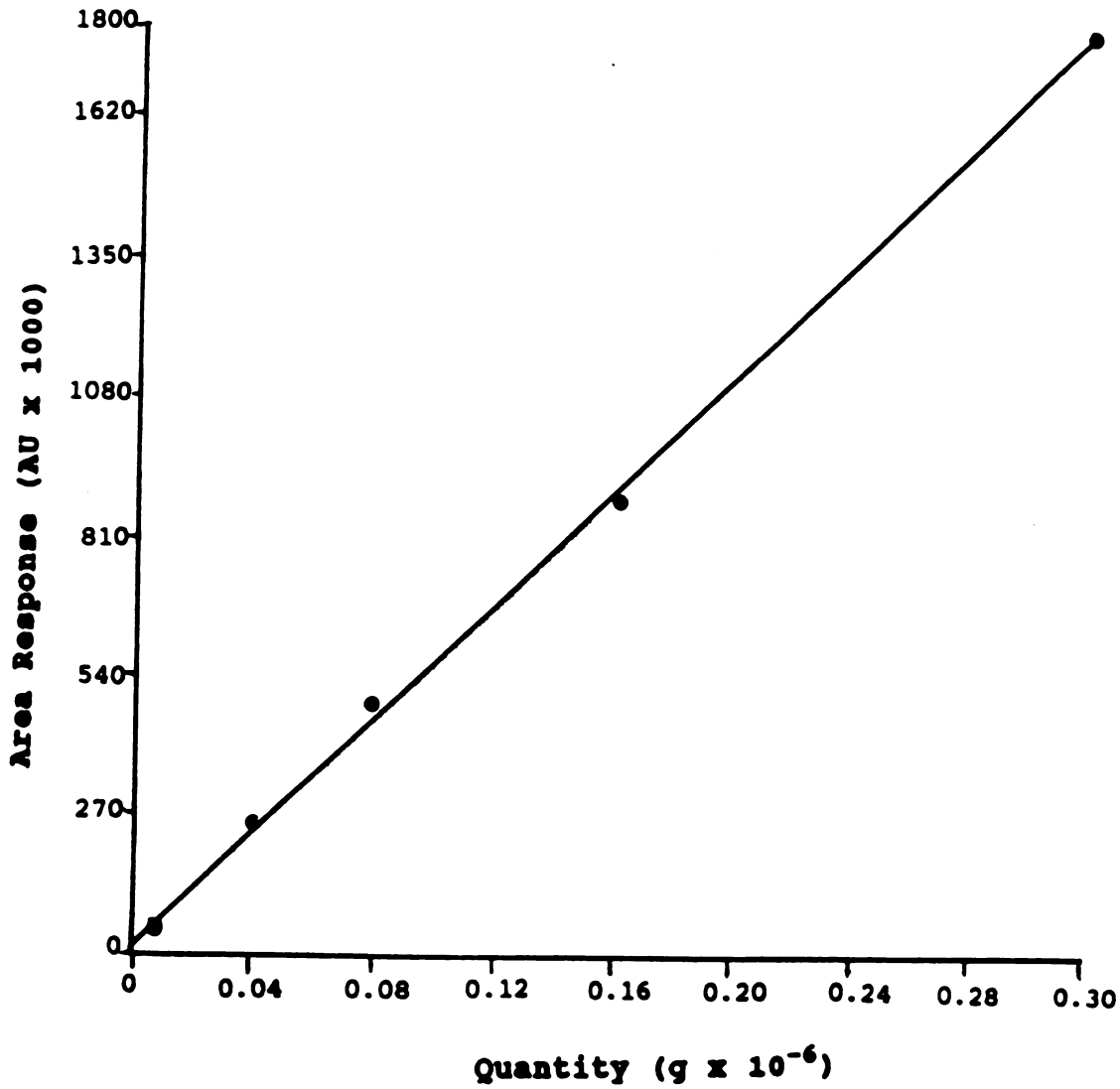

Figure 29. Calibration curve of 2-methyl propanol for headspace and diffusion trapping methods

Appendix A (cont'd)

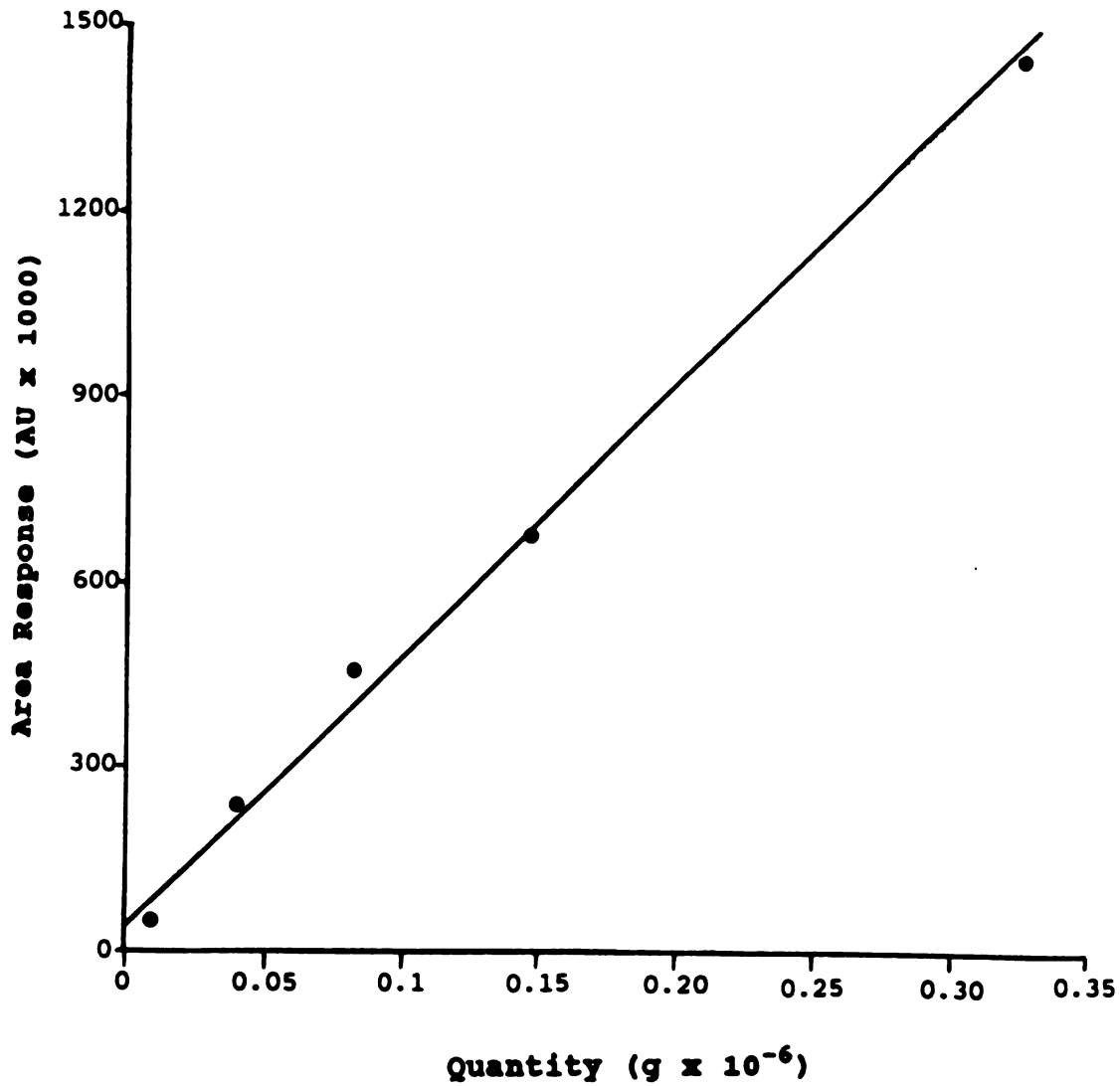

Figure 30. Calibration curve of n-butanol for headspace and diffusion trapping methods

Appendix A (cont'd)

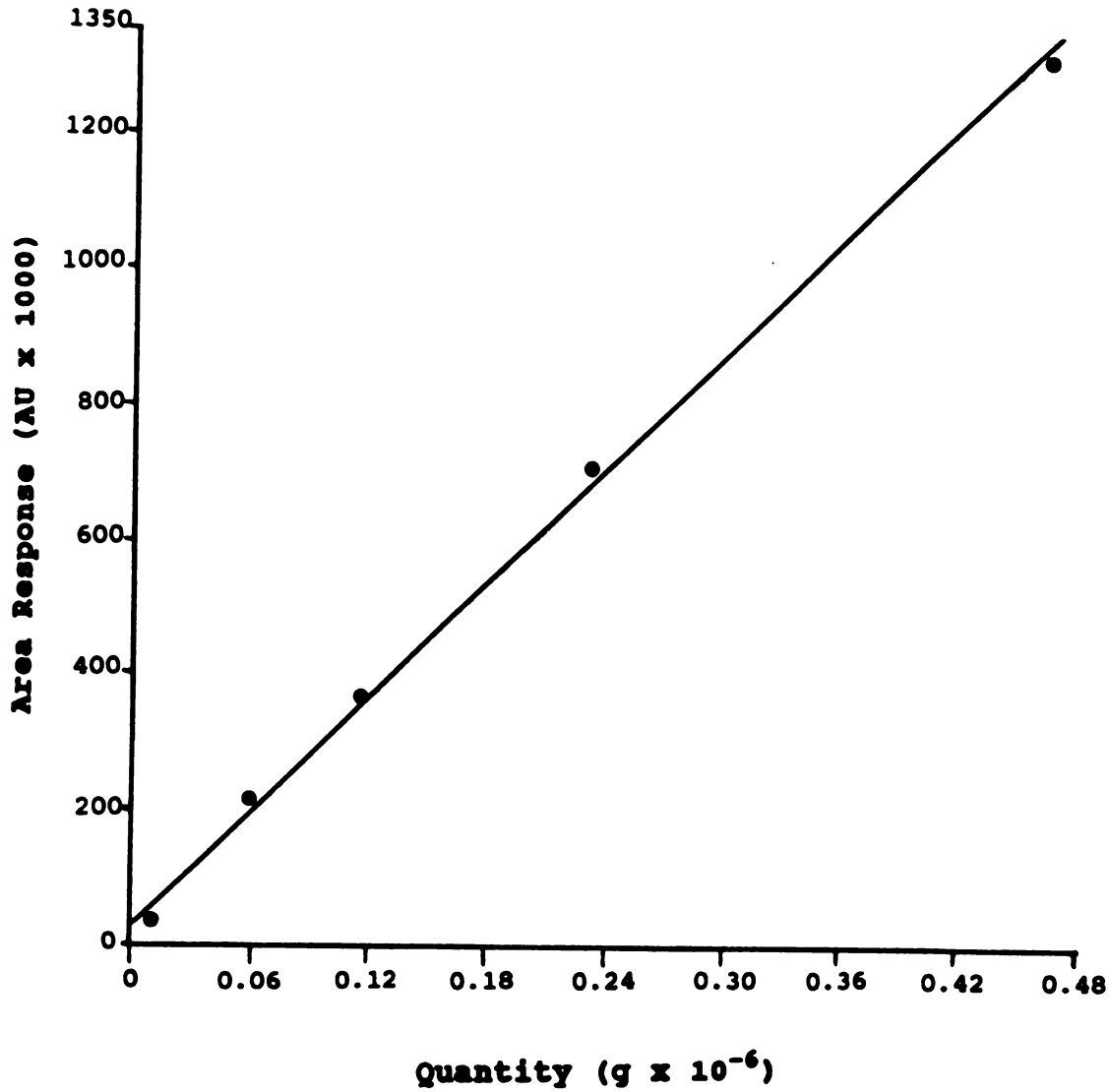

Figure 31. Calibration curve of styrene for headspace and diffusion trapping methods

Appendix A (cont'd)

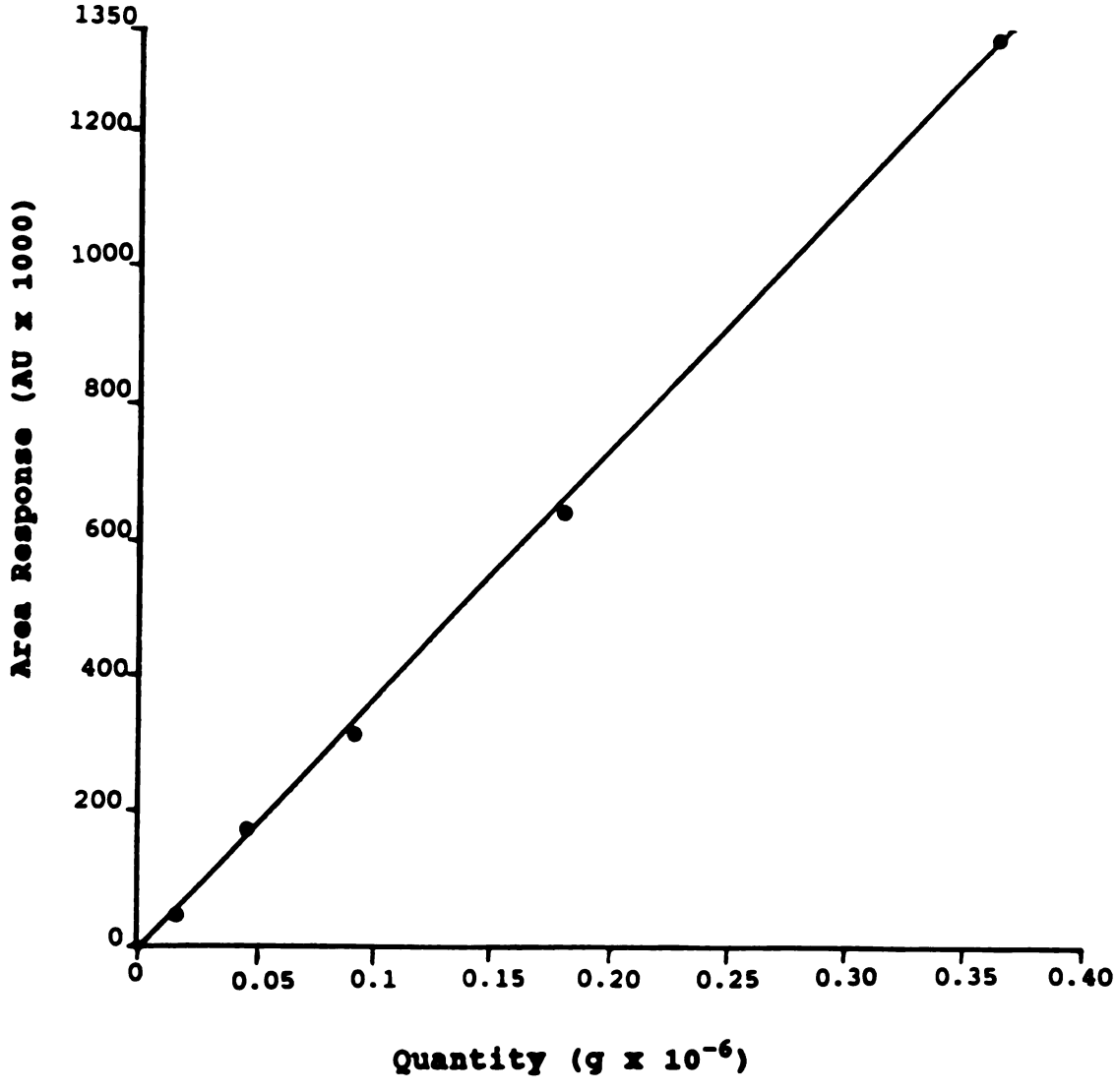

Figure 32. Calibration curve of 2-butoxy ethanol for headspace and diffusion trapping methods

Appendix A (cont'd)

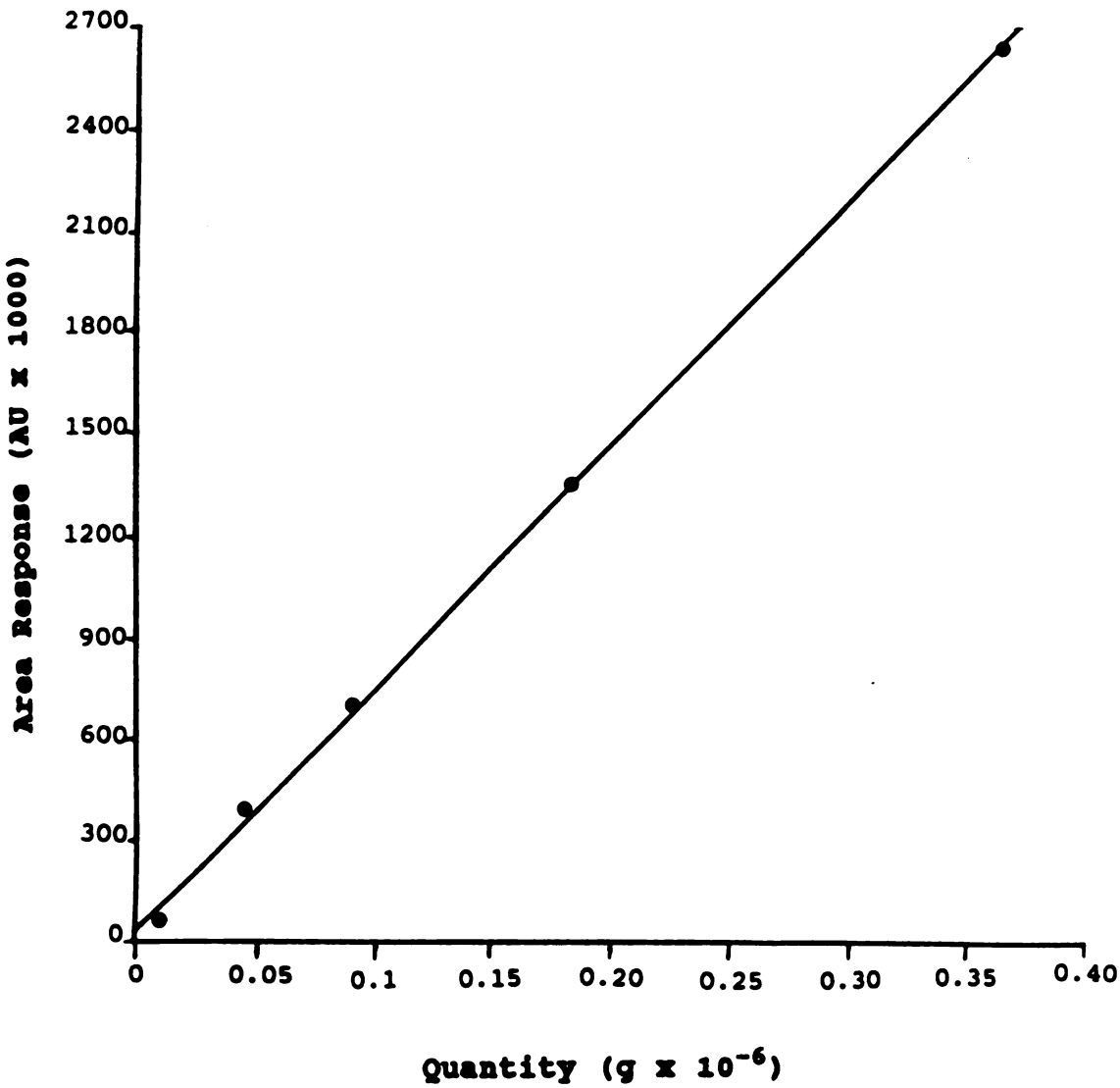

Figure 33. Calibration curve of furfural for headspace and diffusion trapping methods

Appendix A (cont'd)

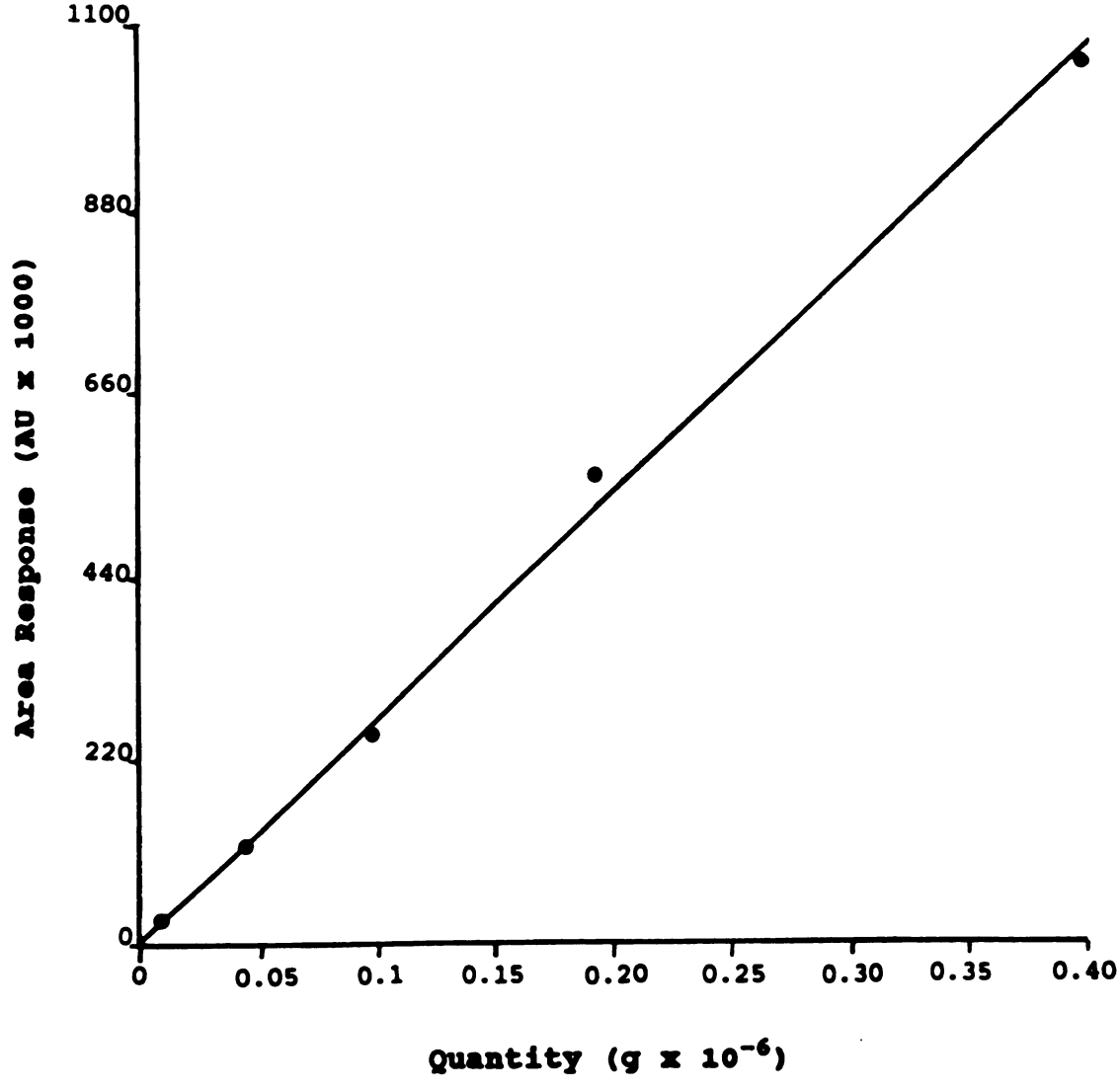

Figure 34. Calibration curve of 2-(2-butoxyethoxy)ethanol for headspace and diffusion trapping methods

Appendix B

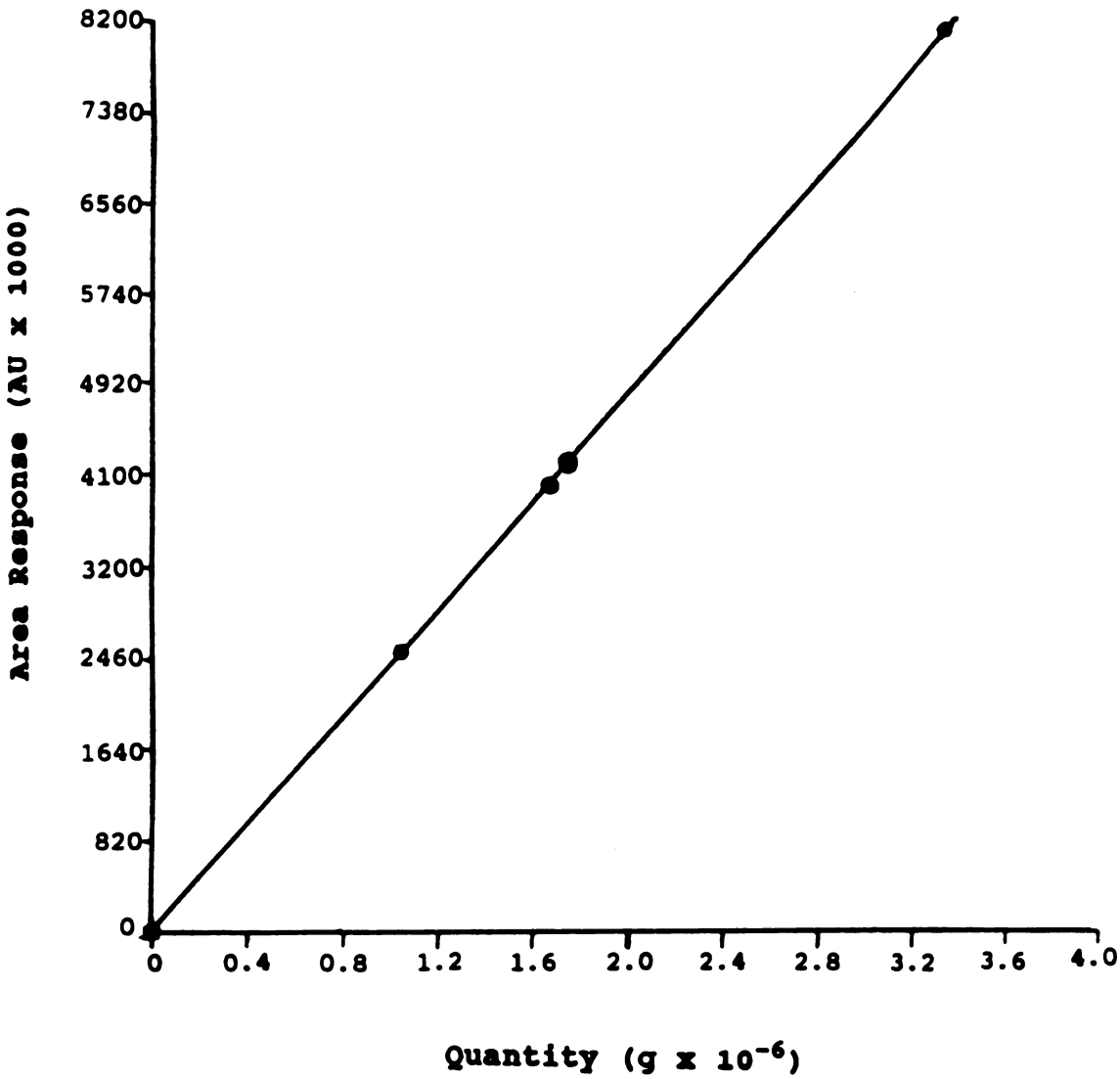

Figure 35. Calibration curve of 2-methyl-propanol for thermal desorption technique

Appendix B (cont'd)

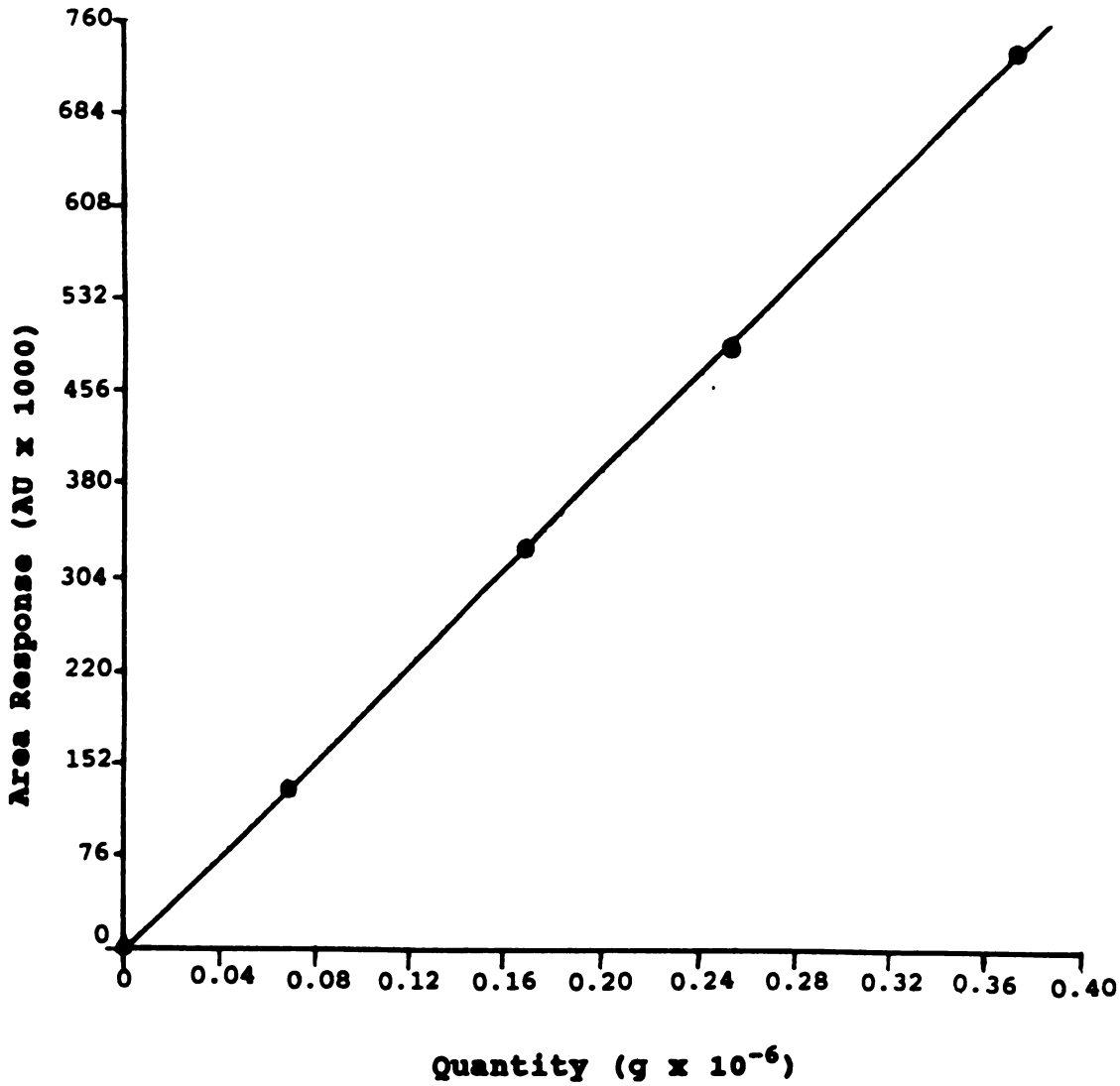

Figure 36. Calibration curve of n-butanol for thermal desorption technique

Appendix B (cont'd)

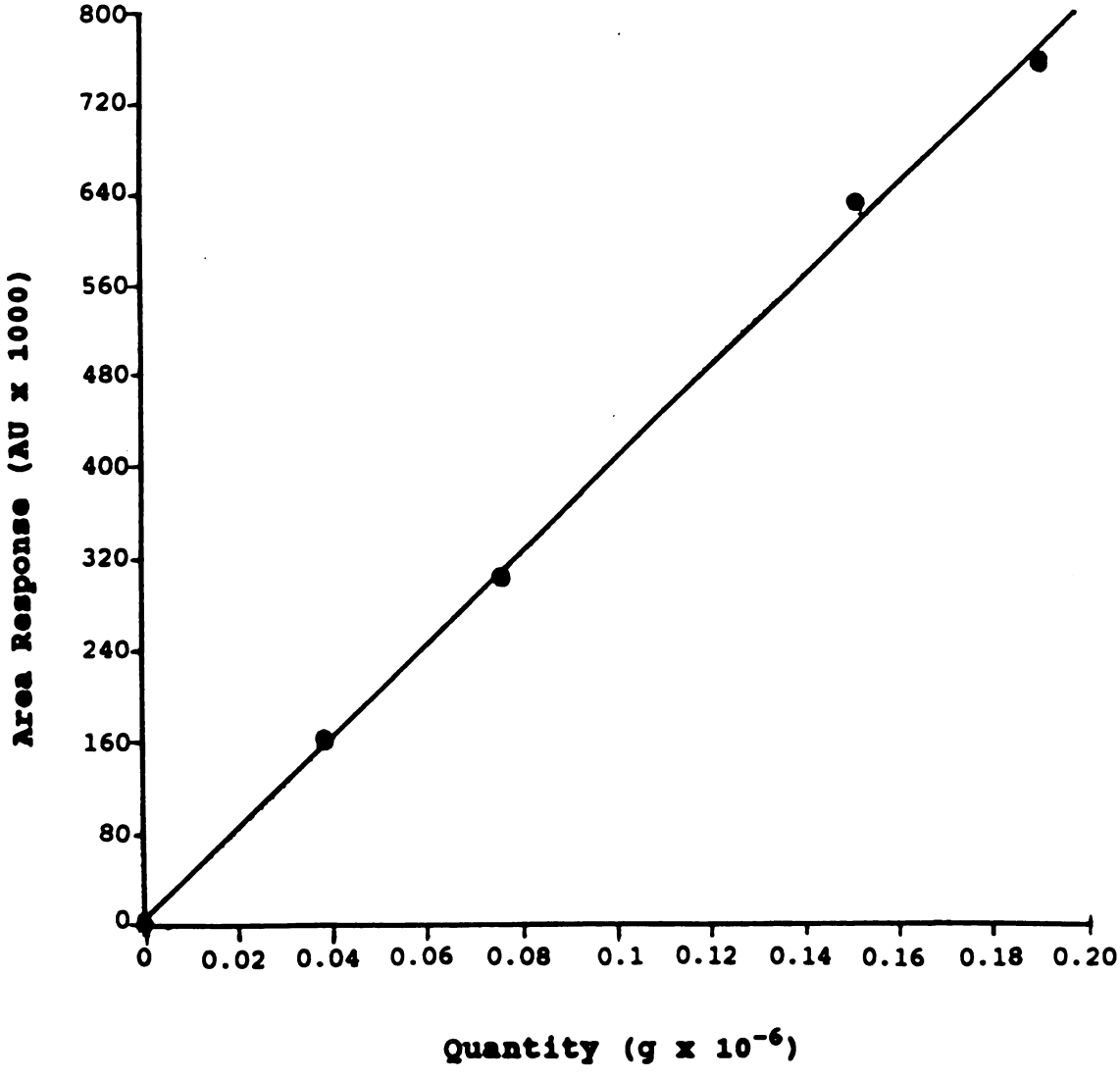

Figure 37. Calibration curve of styrene for thermal desorption technique

Appendix B (cont'd)

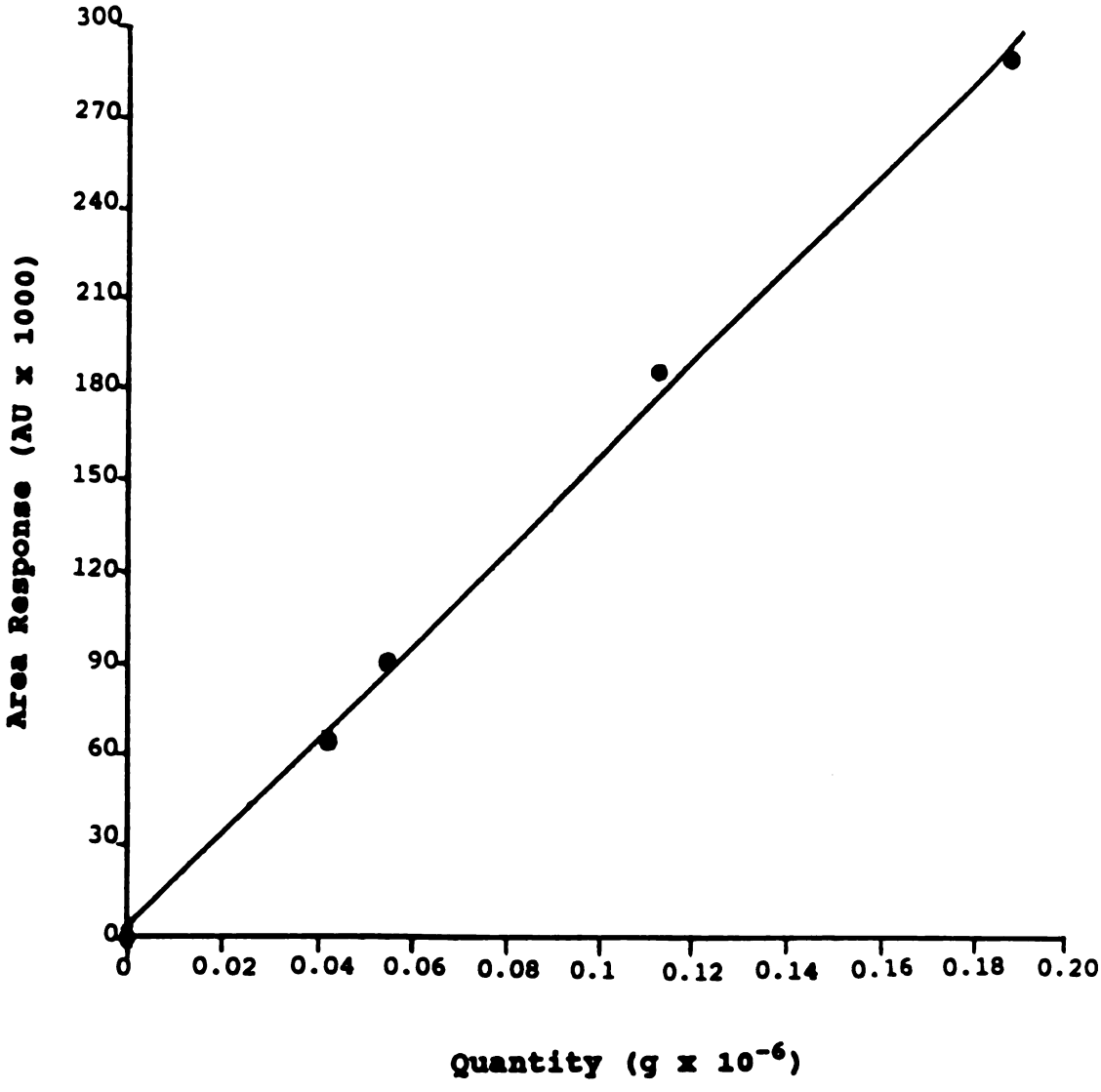

Figure 38. Calibration curve of 2-butoxy ethanol for thermal desorption technique

Appendix B (cont'd)

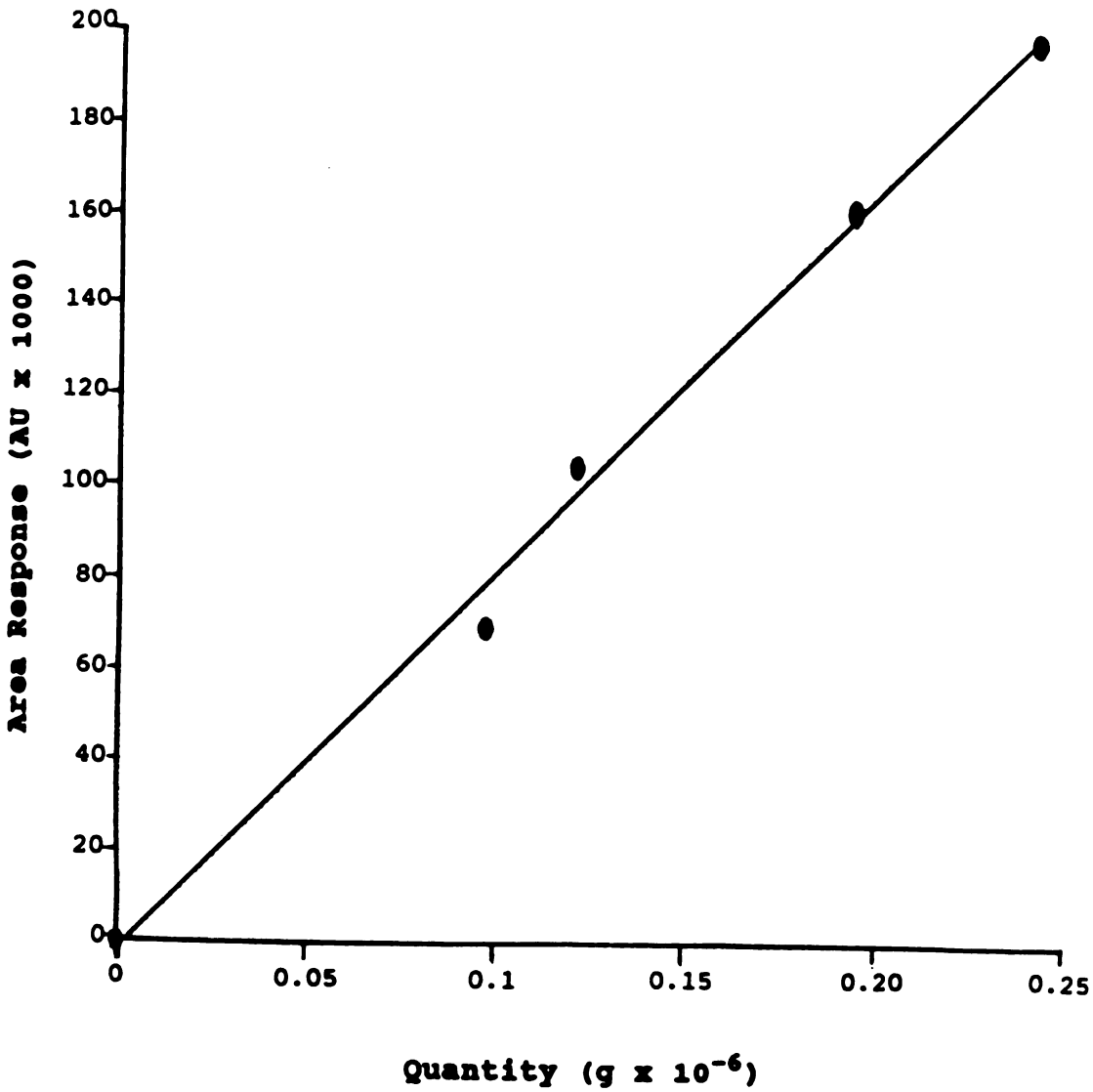

Figure 39. Calibration curve of furfural for thermal desorption technique

Appendix B (cont'd)

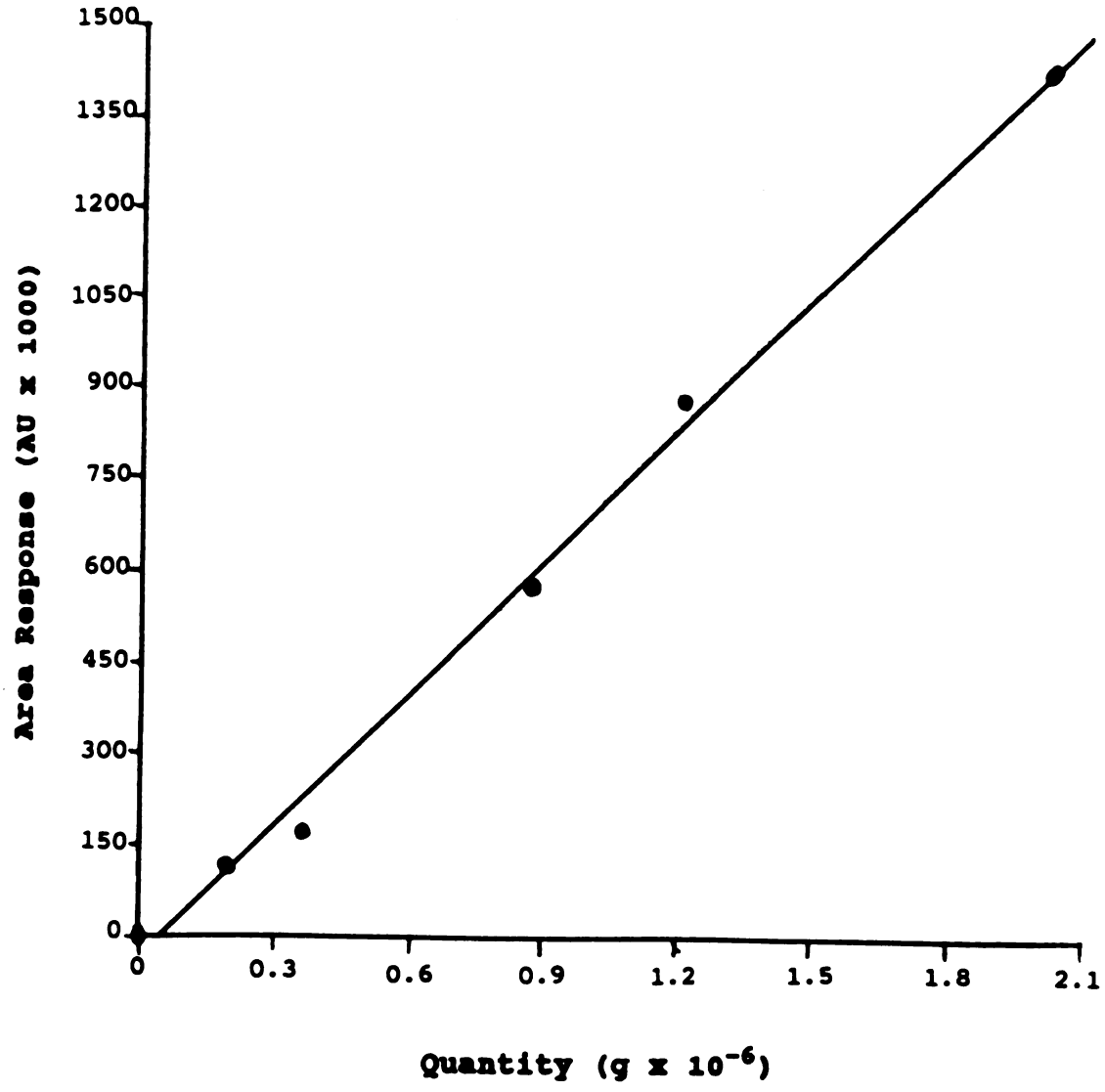

Figure 40. Calibration curve of 2-(2-butoxyethoxy)ethanol for thermal desorption technique

APPENDIX D

Sample calculation used for converting area response units into micrograms of analyte per gram of susceptor (μg/g) in the diffusion trapping technique.

$$Concentration(\mu g/g) = \frac{CF \times R_s}{W}$$

CF = Calibration factor

R_s = Area response of sample

W = Sample weight

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