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IDENTIFICATION OF RESIDUAL ORGANIC COMPOUNDS IN FOOD PACKAGES

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SUMMARY

Residual organic compounds in laminated plastic material used in food packages have been identified through gas chromatographic and gas chromatographic-mass spectrometric analyses of solid samples using a simple apparatus and direct headspace sampling of vapors from heated samples. Preliminary studies show no decomposition of components at evolution temperatures between 30 and 125°C. Although recovery of residual components was much less than 100% at all temperatures, reproducibility based on peak areas was 19–53% relative standard deviation with 10–30 μg/g with no sample pretreatment. Various volatile organic compounds including methanol, 1-ethoxy-2-propanol, 1-propanol, 2-(2-hydroxypropoxy)-1-propanol, *n*-propyl acetate, 2-methyl-2-propanol, *tert.*-butanol and a C_9H_{20} hydrocarbon were identified in samples of laminated plastic material.

Using a Tenax trap and the above technique these components were also detected in the vapor phase inside sealed bags made from the same material. Application of this technique to analysis of vapors in commercial potato chip packages revealed the presence of benzene as a major constituent.

INTRODUCTION

Organic compounds which promote stability and appeal of food products are often added to foods during various stages of processing. Occasionally other organic compounds may be present inadvertently as residues from the manufacturing process. Such compounds include methylene chloride and trichloroethylene in coffee[1] and fluorocarbons in frozen seafood[2]. Similar volatile organic compounds may also be present originally in the packaging material, but these contaminants may later migrate into the packaged food. Examples of this type of contamination include vinyl chloride in corn oil[3], styrene in meats[4] and plasticizers in yogurt[5].

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Although the determination of these and other volatile contaminants in actual food samples is difficult, analyses of packaging materials and the vapor phase inside sealed packages may be useful in the quality control of such contaminants in plastics and also for preliminary screening of offensive odors and tastes in foods. Since packaging materials often contain a mixture of volatile organic compounds, most methods for the determination of residual contaminants have been based on gas chromatographic techniques. Most methods of analysis involve headspace sampling, although various techniques differ in sample preparation. Typically, a portion of the sample is dissolved in solvents such as dimethyl formamide, isopropanol or diethyl ether, and the solution is sealed in a glass container which is equipped with a septum. The container is placed in a heated bath at 70–80°C for 1–2 h and a portion of the headspace is then removed and analyzed using gas chromatography (GC). Examples of this method include methylene chloride in polycarbonates[6] and plasticizer in 2,4-diacetate cellulose[7].

Wilks and Gilbert[8] described a method for the determination of residual volatile solvents in packaging materials using GC analysis of headspace samples of solid materials. However, only samples which were spiked with known amounts of certain compounds were analyzed. Headspace analysis using solid samples has also been applied to synthetic rubbers[9], vinyl chloride in polyvinyl chloride[10] and residual hydrocarbon solvent in polyacrylic acid[11].

Laminated packages which consist of two sheets of plastic held together with an adhesive or glue have been widely used in the snack food industry. These materials have excellent properties for retention of odor and flavor, protection from moisture and adaptation to automated packaging. However, if the laminated material is not properly dried, residual solvents may be present in the final food packages. This paper describes results from a simple and rapid headspace method which has been developed for the determination of trace concentration levels of volatile organic compounds in laminated and other packaging materials and in vapor samples from inside sealed packages.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard Model 5830A gas chromatograph was equipped with a 2 m × 2 mm I.D. glass column containing 2 % OV-7 on Aue packing[12], a flame ionization detector (FID), a heated four-port, gas-switching valve (Valco, Houston, TX, U.S.A.) and a flash desorption oven. Sample tubes were attached to the four-port valve using 0.635–0.159-cm Swagelok reducing unions (Niagara Valve and Fitting, Hamilton, Canada) and 0.635-cm I.D. Vespel ferrules (Chromatographic Specialties, Brockville, Canada). The aluminium flash desorption oven was heated using two 500-W heating cartridges (Watlow, St. Louis, MO, U.S.A.). The final design is shown in Fig. 1. Conditions of analysis were: initial temperature, 0°C; temperature program rate, 10°C/min; final temperature, 150°C; injection port temperature, 250°C; detector temperature, 275°C; slope sensitivity 0.1 mV/sec; area reject, 1000; attenuation, 64 or 128; carrier gas, helium; flow-rate of carrier gas, 30 ml/min; temperature of gas valve, 200°C and temperature of transfer lines, 180°C. Conditions for headspace sampling are specified when necessary.
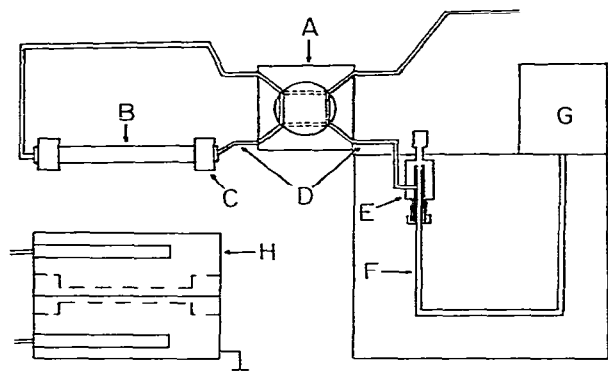
Fig. 1. Final design of desorption apparatus for solid headspace analysis. Details of the apparatus include; A = heated gas-switching valve; B = steel sample-containing tube; C = Swagelok fittings; D = 1.58-mm O.D. stainless-steel tubing wrapped in heating tape; E = GC inlet; F = GC column; G = FID or MS; H = thermal desorption oven.

A Model 5992A gas chromatograph–mass spectrometer was equipped with a single flexible disc, x–y plotter, membrane separator and thermal desorption system as described above. The chromatographic column was the same as described above. Conditions for analysis by GC–MS were: initial temperature, $-30°C$; temperature program rate, $10°C$/min; final temperature, $150°C$; lower mass range, 25 a.m.u.; upper mass range, 400 a.m.u.; scan rate, 330 a.m.u./sec; electron multiplier voltage, 1800 V; mass peak detection threshold, 2; and GC peak detection threshold, 300. The temperature of the gas-switching lines and transfer lines was approximately $60 \pm 10°C$ and the temperature of the flash desorption oven was $80°C$. The total time of heating samples was 3 min including a 2-min period for preheating. Software used in these GC – MS analyses was supplied by the manufacturer and modified by Dickson[13].

Preparation and analysis of samples

Packaging material. Plastic samples (approx. 7 cm^2) were cut using scissors and weighed to ± 0.001 g. Various samples were taken from center sections of unused sheeting, sealed but unfilled bags and bags which contained food products. A square of sample was then rolled and inserted into an empty stainless-steel tube with dimensions 7.6 $\times$ 0.64 cm O.D. $\times$ 0.41 cm I.D. The sample-containing tube was attached to the switching valve while the valve was in the by-pass position (position 1). In GC analyses of the packaging materials, the tube was heated with the flash desorption oven for a time while the valve was still in position 1. After this preheating period the valve was switched to divert the carrier gas through the tube and into the inlet of the gas chromatograph (position 2). After an additional 1 min the valve was returned to position 1 and the oven was removed from the tube. When the valve was switched in this last step the temperature program was started.

In GC–MS analysis a similar procedure was followed except residual air in the transfer lines and the tube was minimized by a 15-sec flush of the desorption system while the tube containing the sample was at ambient temperature and the GC

column was at 50–80°C. Following this step to remove air from the desorption system, the analysis was continued as described above.

Vapor samples. Vapor samples were prepared by drawing the headspace inside sealed packages through tubes containing Tenax-GC (Applied Science Labs., State College, PA, U.S.A.) sorbent material. Both empty and filled packages were used in these analyses. Each tube contained approximately 100 mg of Tenax-GC. A gentle vacuum was applied to one end of the trap using an aspirator while a needle attached at the other end of the trap was used to puncture the bag. A sharp No. 11 gauge needle fitted in a 0.635–0.318-cm Swagelok reducing union was used in this step, and the seal between the bag and needle was surprisingly good under these conditions. The traps were analyzed by GC and GC–MS using procedures described above.

Reproducibility and effects of time and temperature

The effect of temperature on the amounts of components released from samples of laminated plastic sheeting was examined using five desorption temperatures. These temperatures were: 30, 55, 77, 95 and 125°C. The total time of desorption was 3 min including a 2-min time for preheating. Peak areas were converted to concentrations using integration values, sample weights and an average response factor of 400 area counts/ng for the FID. In a similar study the effect of preheating time on amounts of components released was studied at a desorption temperature of 85°C using four values for preheating time. These values, exclusive of the 1-min period for sweeping organic compounds into the inlet of the gas chromatograph were: 1, 2, 5 and 10 min.

Triplicate analyses of samples of laminated material which were cut from similar sections of unused plastic sheeting were used to determine the reproducibility of the technique. The temperature of the desorption oven was 80°C while the time of desorption was 3 min.

RESULTS AND DISCUSSION

Analysis by GC

Results from studies on the effect of temperature on amounts of components which are released from laminated material are shown in Figs. 2 and 3. Gas chromatograms are presented as bar plots[14] from five analyses at different temperatures using thermal desorption techniques. A full-scale value of 30,000 area counts was chosen for use in each plot of Fig. 2 for convenient visual comparison. The plot in Fig. 2A shows that the vapor-phase above the solid laminated plastic contains at least 18 major and minor components. No detectable amounts of volatile organic components were found in chromatograms of blank analyses. In the blank analyses, identical conditions were used except the sample was omitted. The plots in Fig. 2A–E illustrate the magnitude of differences in absolute concentration of individual components among analyses. Actual concentrations of all organic compounds for the different temperatures were: 30°C, 1.9 μg/g; 55°C, 11.5 μg/g; 77°C, 21.9 μg/g; 95°C, 85.8 μg/g; and 125°C, 491.1 μg/g. Although these results show considerable quantitative differences, the distribution of components in each plot was similar and no major new components were detected at higher temperatures. Therefore, no thermal decomposition of the laminated materials was evident using the conditions of this study.
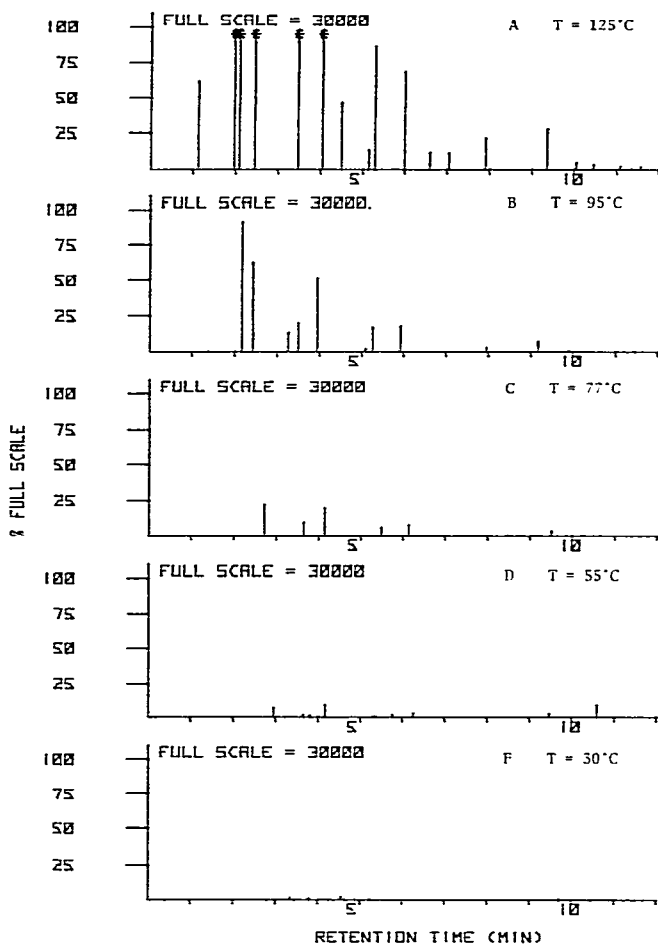
Fig. 2. Bar plots from GC analyses of laminated plastic material using five desorption temperatures.

The relative quantitative differences for organic compounds in each analysis are shown by plots in Fig. 3A–E. Although the data used in Fig. 3A–E are the same as in Fig. 2A–E, the full-scale values have been normalized to the area count for the most abundant component in each plot. With a thermal desorption temperature of 30°C, the major component eluted near the middle (4.6 min) of the chromatogram. A later eluting component (9.6 min) was approximately 70% in abundance of the major component. The abundance ratios of various components differed at each desorption temperature. At a 125°C desorption temperature the major component was an early eluting (1.9 min) component. Furthermore, the compound which was the major component at 30°C was only 25% of the new major component (3.5 min) at 125°C. Another large change in relative concentration was seen for a later eluting component which decreased from 68% (30°C) to 5% (125°C) of the most abundant compound. While other differences are discernable in these plots, three features characterize the results: the presence of volatile organic compounds in the vapor phase, even at 30°C;
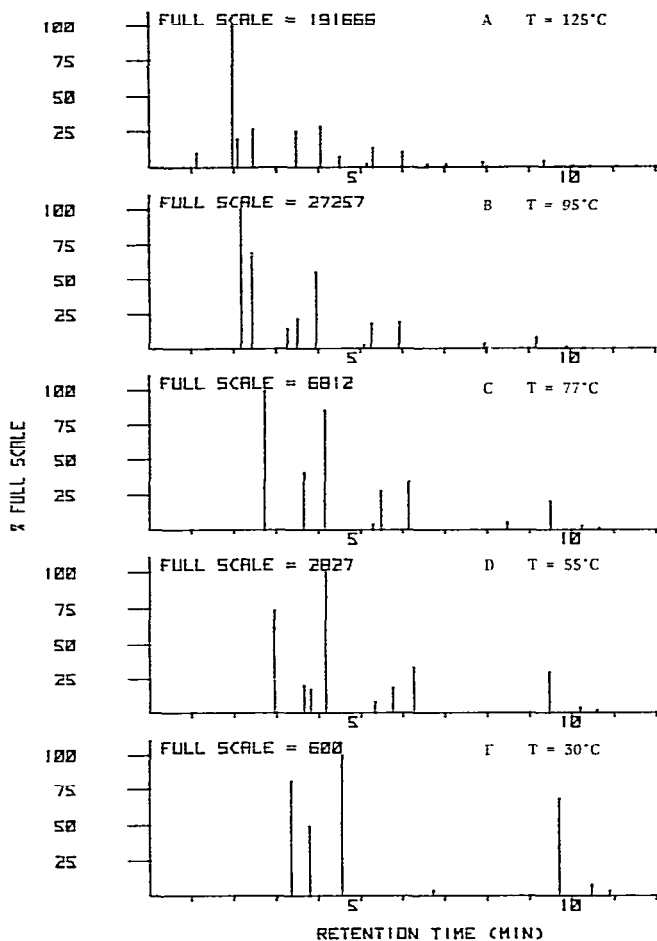
Fig. 3. Bar plots from Fig. 2 with full-scale values normalized to largest component in each plot.

large amounts of organic compounds in the laminated material; and the shift at higher desorption temperatures to lower-retention-time components.

The presence of organic compounds in the vapor phase at 30°C was not un-expected since odors had been associated with the packaging material. However, the concentration of these components showed that the composition of the sample was changing daily and that the drying process was incomplete. Clearly, when charac-terizing a particular batch of material, long storage times may alter the quantitative results.

Variations in retention times as large as 1.5 min for the early eluting com-ponents were observed. Since the components are condensed at the inlet of the column, events which occur before this thermal focusing step are not expected to influence retention times.

Although the causes for these differences have not been determined, large concentration changes which exceed the linear range of the distribution isotherms

may result in reduced retention times. This behavior is particularly evident when low capacity ($\leqslant 2\%$ liquid phase loading) columns are employed.

When the total concentration of components in the headspace is plotted *versus* desorption temperature using the above data, the curve shows no evidence that the system was reaching an equilibrium value. This was supported by a second study where times for preheating as long as 10 min were used with desorption temperatures of 85°C. The total amounts of material which were released during these analyses were: 1 min, 22.0 μg/g; 2 min, 32.0 μg/g; 5 min, 97.0 μg/g; and 10 min, 210 μg/g. The results from these experiments also showed that total recovery of the volatile compounds from laminated material was incomplete using the above conditions. However, the reproducibility of quantification for a specific preheating time and desorption temperature based on peak areas had a range for a relative standard deviation of 15–53 % with a median value of 22 %. These data from replicate analyses are given in Table I and include the total measure of precision from sample handling, headspace sampling and GC analysis with thermal focusing. Although numerous aspects of quantification such as preparation of standards, storage of samples and calibration of response for particular analyses still require development, some progress has been made in quantitating similar methods. Kalb[15] has used a "discontinuous gas extraction" procedure and found that his procedure was useful in the determination of solvents in printed foil, but was too time consuming for routine analyses. Others[16] have measured amounts of volatile components in solids through the use of Henry's constant which was determined for experimental conditions. Another alternative reported by Kalb[15] is the use of reference materials with known compositions that were predetermined using dissolution methods.

TABLE I

VALUES FOR REPRODUCIBILITY OF GC HEADSPACE ANALYSIS OF LAMINATED MATERIAL

Retention time (min)		Estimated concentration (ng/g)	
Average	Standard deviation	Average	Standard deviation
2.43	—	15091	2891
3.33	0.04	4340	710
3.80	0.06	8538	1814
4.95	0.04	395	90
5.13	0.04	2892	599
5.82	0.02	3371	1237
7.87	0.08	695	366
9.24	0.05	2891	447
9.97	0.05	338	131
10.38	0.04	189	46

Analysis by GC–MS

Samples of both laminated plastic material from a food package and the vapor phase inside the same package were analyzed using GC–MS techniques. Results from these analyses are shown in Figs. 4 and 5. In Fig. 4, the total ion chromatogram (TIC) is shown from an analysis of a 0.138-g sample of packaging material. The number and
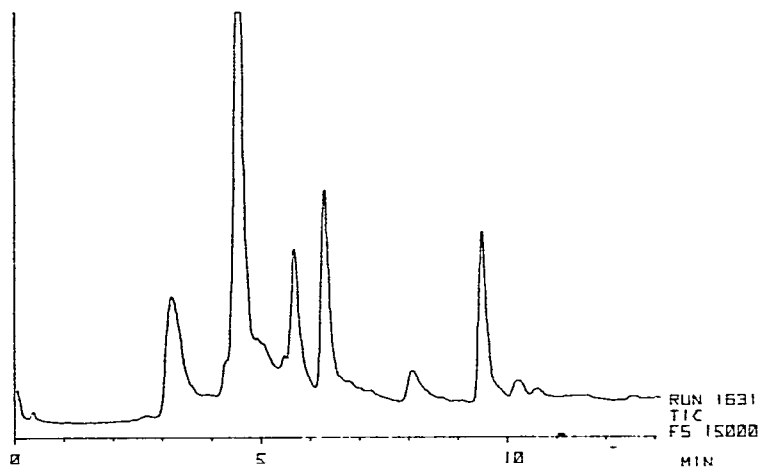
Fig. 4. Plot of TIC from GC–MS analysis of solid laminated material. Conditions of analysis given in text.

distribution of components in this TIC compare favorably with patterns which are shown in Figs. 2 and 3 from analysis of the same material using GC. Furthermore, the relative abundances of the various components were also very similar to those found by GC analyses. The TIC consists of six major components with another seven minor components or shoulders on other peaks. These components were identified using mass spectra which were then compared to reference spectra from the Environmental Protection Agency/National Institute of Health reference volumes[17]. The first four major components were esters or alcohols while the last major component was a C_9H_{20} branched hydrocarbon. The identity of these and other components are listed in Table II, although an exact structure for this C_9H_{20} was not determined. In Fig. 4 a very small amount of air was detected at an elution time of 0.4 min. This shows that switching the valve for 15 sec to force carrier gas through the sample tube and carrier

TABLE II

COMPONENTS IDENTIFIED USING GC–MS ANALYSIS OF LAMINATED PACKAGE SYSTEMS

From Figs. 4 and 5.

Retention time (min)	Component	Package material	Vapor phase
2.7	Methanol	×	×
3.2	1-Ethoxy-2-propanol + second unidentified component	×	×
3.8	Methyl ethyl ketone		×
4.3	1-Propanol	×	
4.5	2-(2-Hydroxypropoxy)-1-propanol	×	×
5.6	n-Propyl acetate	×	×
6.3	2-Methyl-2-propanol + trace of toluene	×	×
8.1	tert.-Butanol	×	×
9.5	C_9H_{20}	×	×
10.2	C_9H_{20}	×	×
10.6	C_9H_{20}	×	×

lines was sufficient to sweep most of the residual air from the desorption system and to prevent excessive amounts of air to enter the mass spectrometer. The initial temperature of $-30°C$ resulted in a separation time of about 2.5 min between air and methanol.

Results from GC–MS analysis of the vapor phase inside two packages used in the above analysis are shown as a TIC in Fig. 5. The pattern of this TIC is nearly qualitatively identical with the TIC shown in Fig. 4. Most components in the gas phase were the same as in the laminated material and retention times were close or identical matches. Also the relative abundances of components in the gas phase were similar to those from GC headspace analysis of the plastic material. A single major difference between Figs. 4 and 5 is a sizable component which eluted at 3.8 min in Fig. 5. This component was identified as methyl ethyl ketone using mass spectra.
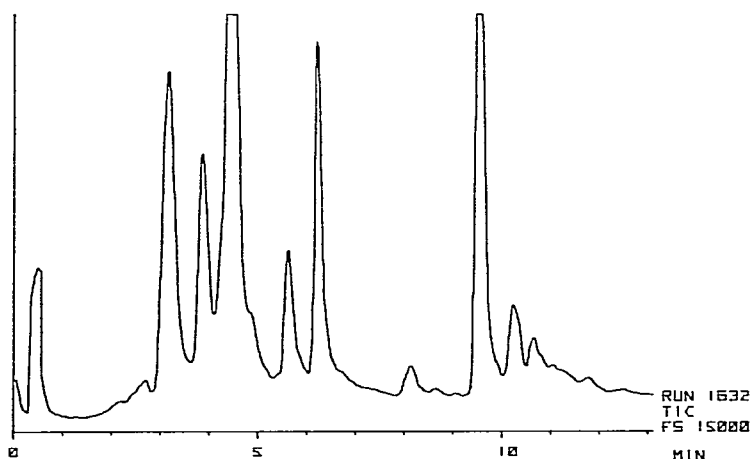

Fig. 5. Plot of TIC from GC–MS analysis of vapor phase inside two sealed bags made from laminated material. Conditions of analysis given in text.

These methods were applied to analysis of both the vapor space and plastic material of commercial potato chip bags. Typical results are shown in Figs. 6 and 7. The packaging material used in these analyses was a smooth white flexible plastic, perhaps polyethylene or polypropylene, which was used as a package for potato chips. Results from GC–MS analysis of the white plastic are shown in Fig. 6 as a TIC. Very few components were detected in this analysis and concentrations were estimated to be less than 10 $\mu g/g$. These components were mostly branched or unsaturated hydrocarbons. However, GC–MS analysis of the vapor phase inside these bags showed a very different composition. Only a single major component was detected in the vapors, and the component was clearly identified as benzene. Varying amounts of benzene were found in replicate analyses of similar packages. The amount of benzene present in the vapor phase of two bags was more than sufficient to overload the GC–MS. In Fig. 7 the distortion of the peak is a result of the mass spectrometer being automatically turned off when excessive amounts (> $ca.$ 10 μg) of components enter the mass spectrometer.
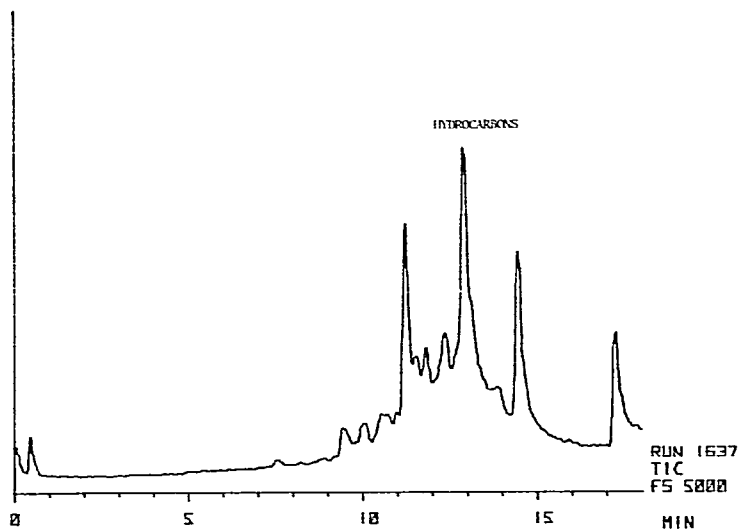
Fig. 6. Plot of TIC from GC–MS analysis of white homogeneous solid material used in potato chip bags.
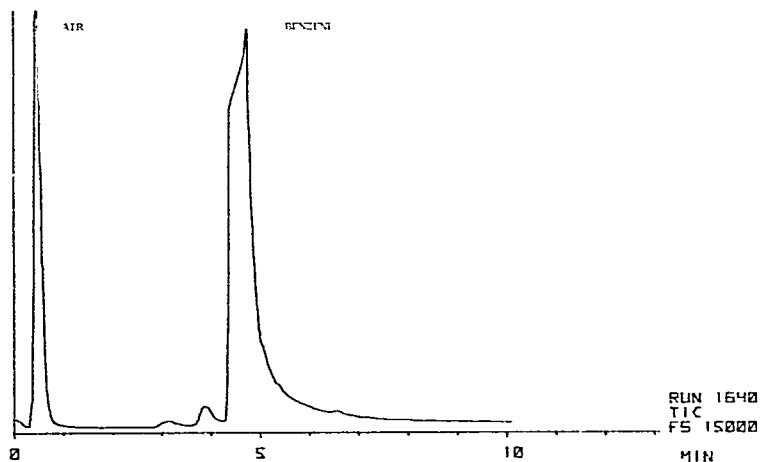

Fig. 7. Plot of TIC from GC–MS analysis of vapor phase inside two potato chip bags.

The origin of the benzene is unknown, since it could have been introduced at any point in the product preparation or in pressurization of the bag. A more complete study is underway to determine the extent and concentration of benzene and other components in this type of packaging system.

ACKNOWLEDGEMENT

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