

Toward an Optimized Dynamic Headspace Method for the Study of Volatiles in Low-Density Polyethylene

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A dynamic headspace technique for detecting C₆–C₁₄ volatile organic compounds (VOCs) in low-density polyethylene (LDPE) is discussed in which VOCs are purged with N₂, trapped at ambient temperatures on Tenax-GC, and identified by gas chromatography/mass spectrometry. The experimental variables are quantitatively modeled to enhance sensitivity of the technique. The rate of extraction of VOCs from LDPE and the rate of isothermal desorption of VOCs from Tenax-GC are first-order processes with rate constants of 2.79×10^{-5} and $1.53 \times 10^{-3} \text{ s}^{-1}$ respectively. Approximately 4.2% of extractable VOCs are present in the vapor phase at ambient temperature, and 21% of VOCs are liberated instantaneously from Tenax-GC during thermal desorption at 200 °C. The chromatographic peak area associated with each VOC, and the total peak area in the chromatographic window, vary with desorption temperature in accordance with the van't Hoff isochore with an "average" desorption enthalpy of 45.5 kJ mol⁻¹.

Keywords: *Low-density polyethylene (LDPE); dynamic headspace sampling; gas chromatography/mass spectrometry (GC/MS); volatile organic compounds (VOCs); Tenax-GC; purge and trap; mathematical modeling*

INTRODUCTION

Low-density polyethylene (LDPE) has widespread use in food-packaging applications due to its strength, low density, low cost, and ease of processibility (Tou et al., 1990). Approximately 65% of all LDPE produced is used for film production, and a large proportion of film is used for food packaging (Bakker, 1984). The processing of LDPE involves the application of high temperatures and shearing stresses which, combined in the presence of oxygen, usually cause thermal and oxidative degradation of the polymer (Kim and Gilbert, 1989; Kim-Kang, 1990). Appreciable levels of polyethylene (PE) degradation can occur, even under mild conditions (Al-Sammerai and Al-Nidway, 1989; Grassie and Scott, 1985), and so degradation products can be produced at all stages in the life cycle of the polymer including fabrication, processing, storage, and transportation. Small concentrations of degradation products entrained within the polymer are of concern to the food-packaging industry as these contaminants may compromise the quality of packaged foodstuffs (Kaljurand and Smit, 1994).

The transfer of organoleptically active compounds from PE to packaged foodstuffs is widely reported in the literature (Bigger et al., 1996), and such compounds are regarded as being difficult to measure (Fales et al., 1983). The most widely used methods for the analysis of volatile organic compounds (VOCs) originating from PE are all based on gas chromatography (GC), most commonly gas chromatography/mass spectrometry (GC/MS) (Anselme et al., 1985; Bravo et al., 1992; Bravo and Hotchkiss, 1993; Chuang, 1984; Culter, 1992; Fales et al., 1983; Linssen et al., 1993), with flame ionization

detection GC being used to a lesser extent (Anselme et al., 1985; Bravo and Hotchkiss, 1993; Peled and Mannheim, 1977). There is a variety of techniques that are used in conjunction with chromatographic analysis for the sampling and detection of VOCs. These include supercritical fluid extraction (Nielson, 1991), GC-olfactory detection (Bravo et al., 1992), vacuum distillation (Chuang, 1984), selective volatile extraction (Bravo et al., 1992; Bravo and Hotchkiss, 1993; Kozinowski and Piringer, 1986), water/steam extraction (Culter, 1992), and dynamic headspace GC analysis (Fales et al., 1983; Linssen et al., 1991).

Sampling of VOCs originating from PE is typically performed at elevated temperatures in the range 100–350 °C (Barabas et al., 1976; Bravo et al., 1992; Bravo and Hotchkiss, 1993; Chuang, 1984; Dalbey et al., 1992; Hoff and Jacobsson, 1981; Hoff et al., 1982; McGorin et al., 1987). Surprisingly, few of the sampling methods are designed to study VOCs that are present in PE at ambient temperature (Fales et al., 1983; Linssen et al., 1991). Since the classification of odorous properties of PE is always determined by human olfactory panels at ambient temperatures, it is therefore preferable to isolate odorous VOCs for chromatographic analysis under similar conditions. Although the sampling of the VOCs in plastic materials at elevated temperatures promotes the removal of volatiles (Bailey and Liotta, 1964), it may also conceal the identity of organoleptically active components as a result of the abundance of nonodorous compounds such as saturated aliphatics that are produced under these conditions.

The "purge-and-trap" technique, first described in 1967, provides a useful preconcentration step for sampling VOCs under ambient conditions (Adlard and Davenport, 1983). The technique involves the trapping of VOCs on a chemically inert sorbent followed by thermal desorption and subsequent GC/MS analysis.

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Tenax-GC (2,6-diphenyl-*p*-phenylene oxide polymer) (Van Wijk, 1970) is a porous polymeric sorbent routinely used as a medium for trapping VOCs prior to chromatographic analysis (Novotny et al., 1974) and has already been used for trapping VOCs originating from various polymeric materials (Azuma et al., 1983, 1984; Bigger et al., 1996; Fales et al., 1983; Forrest et al., 1995; Gramshaw et al., 1995; Hagman and Jacobsson, 1989; Hayashi and Matsuzawa, 1993; Kaljurand and Smit, 1994; Kiselkev et al., 1983; Kolb et al., 1984; Linsen et al., 1991; Long et al., 1988). Tenax-GC has an advantage over most other common sorbents in that it possesses a high thermal stability (Novotny et al., 1974; Sakodyskii et al., 1974; Zlatkis et al., 1973) and is chemically inert (Novotny et al., 1974).

In a study of the effect of sampling temperature on the amount of volatiles released from polymer laminates (Eiceman and Karasek, 1981), a 10-fold increase in the amount of material released was observed when the sampling temperature was raised from 30 to 55 °C. Furthermore, a change in the sampling temperature from 30 to 125 °C resulted in >250 times more material being released from the sample, although the increase in sampling temperature produced differences in the relative abundance ratios of the various components released to the vapor phase. Moreover, in their dynamic headspace study of VOCs in polypropylene, Hagman and Jacobsson (1989) noted that the use of long extraction times and large purge volumes favors high recoveries, which is consistent with the basic theory of gas chromatography.

This paper examines each of the experimental parameters used in the dynamic headspace sampling and chromatographic analysis of VOCs isolated from LDPE. Experimental conditions are described that are aimed toward optimizing the isolation, chromatographic separation, and identification of compounds which are organoleptically active in LDPE at ambient temperatures.

MATERIALS AND METHODS

Materials. A film-grade LDPE formulation (density = 0.92 g mL⁻¹, melt index = 20 g min⁻¹ at 190 °C using 2.16 kg of mass) was obtained commercially. The LDPE contained 1000 ppm of erucamide (*cis*-13-docosenamide, a fatty acid amide; Croda Chemicals Ltd.), 1000 ppm of silica (SiO₂, Filchem Ltd.), and 500 ppm of the phenolic antioxidant Irganox 1076 (Ciba Ltd.). Before pelletization, the polymer and additives were compounded in a Brabender Plasticorder at 60 rpm and 180 °C, with a residence time of 5 min. The average pellet mass was 1.42×10^{-2} g.

A series of C₆–C₁₄ hydrocarbons, alcohols, aldehydes, and ketones which encompass the VOCs identified in this study was obtained in the form of standard kits (Polyscience) and was used to develop the dynamic headspace method described herein.

Methods. A 50 g sample of the pelletized polymer was sealed in a glass jar with a screw-top lid that was fitted with inlet and outlet ports (see Figure 1). The vapor volume in the jar containing the charge of pellets was calculated to be 75.3 mL. The jar and its contents were left at room temperature (18 °C) for 0.5 h prior to experimentation. Volatile compounds present in the headspace of the jar were concentrated at 18 °C onto a Tenax-GC trap (Air-Met Scientific Ltd.) by passing ultrahigh-purity N₂ through the jar. The nitrogen was passed through the jar at a constant flow rate of 220 mL min⁻¹ (258 mg min⁻¹), which was measured at 18 °C using a digital flow meter (ADM 2000, J&W Scientific, Folsom, CA). A scavenging ampoule containing Tenax-GC was used to filter the N₂ purge before this gas was admitted to the jar. The VOC trap (sampling ampoule) was positioned in the gas outlet stream

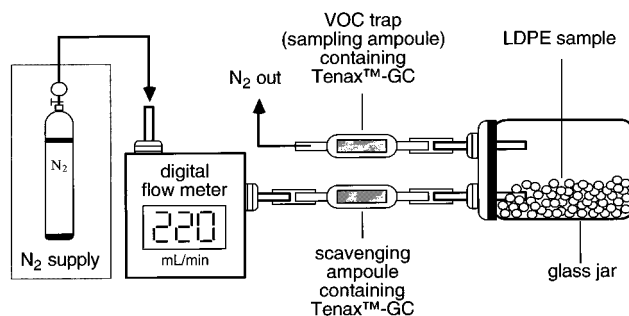


Figure 1. Schematic diagram of apparatus used for purging VOCs from LDPE pellets at ambient temperature.

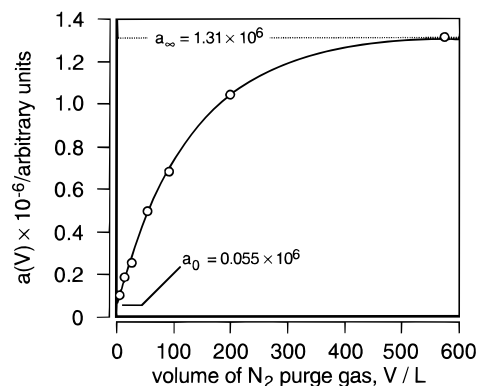


Figure 2. Plot of the total area under the VOC chromatogram in the C₆–C₁₄ region, $a(V)$, versus V , the purge volume (L) of N₂: (circles) experimental data; (solid line) computer-generated fit to the data using parameters derived from the kinetic analysis given in Figure 3. Each exposed Tenax-GC sample was prepared by purging 50 g of pelletized LDPE with N₂, and the VOCs were desorbed at 200 °C for 150 s.

which emerged from the jar (see Figure 1). After the concentration step, the Tenax-GC in the sampling ampoule was transferred to a 20 mL headspace vial and sealed with a silicone septum that was faced with Teflon.

The VOCs were thermally desorbed from the Tenax-GC using a Varian-Genesis automated headspace sampler and were concentrated into a 5 mL sampling loop which was preheated to 220 °C. The contents of the loop were transferred to the chromatographic column of a Varian 3400 GC via a heated transfer line (220 °C). The transfer line back pressure was maintained at 14 psi. The GC was equipped with a fused silica column (DB-5, 0.32 mm × 60 m) containing a cross-linked methylsilicone film of 1 μm thickness (Alltech Associates). A temperature program comprising (i) a 5 min hold at 30 °C and (ii) an increase to 250 °C at 5 °C min⁻¹ was used. The injector was maintained at 215 °C.

Mass spectra were recorded using a Varian-Saturn 2 mass spectrometer with an ion source temperature of 250 °C and an electron multiplier energy of 1850 eV. The mass spectrometer transfer line was maintained at 275 °C. The area counts of the chromatographic peaks were obtained by integration at the 1% peak threshold limit. The assignment of each chromatographic peak was determined using a GC/MS mass spectral library (NIST).

Each point in the plotted results of this study represents one replicate sample that was prepared and analyzed using the above method.

RESULTS AND DISCUSSION

Volume of Purge Gas. Figure 2 is a plot of the total area under the VOC chromatogram in the C₆–C₁₄ region, $a(V)$, versus the volume, V , of N₂ used to purge 50 g of pelletized LDPE. Each sample was desorbed at a temperature of 200 °C in accordance with recommendations made by Fales et al. (1983) concerning the

Table 1. Values of the Parameter ϵ Calculated for Various Studies on VOCs Extracted from LDPE

ref	LDPE sample	VOC formation	mass (g)	V (L)	$V_h \times 10^2$ (L)	ϵ (g ⁻¹)
Azuma et al. (1983)	film ^a	therm oxidn, 80 °C ^c	2	0.6	10	3.0
Bigger et al. (1996)	pellets ^b	therm oxidn, 80 °C	50	13	7.53	3.5
Linssen et al. (1991)	film ^a	ambient sampling	2	2.7	25	5.4
Azuma et al. (1984)	film ^a	therm oxidn, 80 °C ^c	2	3	10	15.0
present study	pellets ^b	ambient sampling	50	200	7.53	53.1
Fales et al. (1983)	pellets ^b	ambient sampling	0.7	14.4	0.654	3146

^a Volume of film assumed to be negligible in calculation of V_h . ^b Pellets assumed to be spherical particles of uniform diameter. ^c Samples exposed to electron beam irradiation.

desorption of VOCs from a Tenax-GC sorbent. A desorption time of 150 s (see also Figure 4) was used in each case.

The results of the N₂ purge experiments indicate that the transfer of VOCs from LDPE to the Tenax-GC trap at ambient temperature increases with increasing purge volume and that ~80% of the volatile phase is transferred using a purge volume of 200 L. To compare this result with the extent to which various systems reported in the literature have been purged, it is important to note that the volume of carrier gas required for the transfer of VOCs is highly dependent on the geometry of the sampling system. A quantity, ϵ , that normalizes the effects of system geometry can thus be defined as

$$\epsilon = V/(V_h m) \quad (1)$$

where V is the volume of purge gas, V_h is the vapor volume in the sampling vessel, and m is the mass of the sample. Clearly, the value of ϵ is indicative of the extent to which a given system has been purged to extract its VOCs. The quantity does not, however, take into account the geometry of the sample as would be necessary, for example, if the efficiency of extraction were to be calculated.

Table 1 lists values of ϵ that were estimated for a range of LDPE volatile extraction experiments described in the literature (Azuma et al., 1983, 1984; Bigger et al., 1996; Fales et al., 1983; Linssen et al., 1991). Although other studies in which VOCs were trapped under ambient conditions have used purged volumes significantly smaller than 200 L, the data in Table 1 indicate that the extent of extraction is not reflected in the purge volume alone. The value of ϵ calculated for the 200 L purge used in the current study is significantly lower than that calculated for the study described by Fales et al. (1983). Moreover, the data in Figure 2 suggest that the extent of extraction is close to quantitative at $\epsilon = 159$ (i.e., ϵ calculated at 600 L), which is still much lower than that which applies in the case of the Fales et al. (1983) study.

The passage of VOCs out of the bulk polymer particles and onto the Tenax-GC trap is presumably a complex process involving several stages. It is likely that the process involves the slow, Fickian diffusion of the VOCs from the bulk of the polymer to the surface, where a rapid, physical desorption takes place. The desorbed VOCs may subsequently diffuse via a moderately slow process into the purge gas stream, where they are swept by this stream onto the trap. In the current work a theoretical treatment of the data shown in Figure 2 was made by assuming that the complex extraction mechanism may be approximated by an overall process in which the rate of transfer of the volatile phase to the trap is proportional to the amount of this phase remaining in the substrate after the sample has been purged for time t_1 . Under these conditions eq 2 applies

$$\partial n(t_1)/\partial t_1 = k_1[n_\infty - n(t_1)] \quad (2)$$

where $n(t_1)$ is the total number of moles of VOCs extracted by the purge gas stream after time t_1 , k_1 is a first-order rate constant for the extraction process, and n_∞ is the number of moles of VOCs extracted by the purge gas after an "infinite" time of extraction.

Integrating eq 2 between the time limits of zero and t_1 yields

$$k_1 t_1 = -\ln[n_\infty - n(t_1)] + \ln(n_\infty - n_0) \quad (3)$$

where n_0 is the total number of moles of VOCs extracted at $t_1 = 0$. Clearly, n_0 is the total number of moles of VOCs present in the gas phase above the substrate initially, and this quantity can be determined from the vertical axis intercept of a plot of $\ln[n_\infty - n(t_1)]$ versus t_1 .

The integrated GC detector response is proportional to the total number of moles of extracted VOCs and for a constant flow rate, ϕ , of purge gas, eq 3 can be rewritten as

$$\ln[a_\infty - a(V)] = -(k_1/\phi)V + \ln(a_\infty - a_0) \quad (4)$$

where V is the volume of purge gas passed through the polymer sample at time t_1 , and a_0 , $a(V)$, and a_∞ are the integrated areas under the chromatogram obtained after the sample is purged for time $t_1 = 0$, $t_1 = t_1$, and $t_1 = \infty$, respectively. Thus, a plot of $\ln[a_\infty - a(V)]$ versus V is linear with a gradient equal to $-k_1/\phi$ (see Figure 3). The quantity $a_1 = a_0/a_\infty$ is the proportion of the total extractable compounds that are present in the gas phase at $t_1 = 0$. Analysis of the data presented in Figure 3 yields $k_1 = 2.79 \times 10^{-5} \text{ s}^{-1}$ and $a_1 = 4.19 \times 10^{-2}$ for LDPE pellets purged with N₂ at ambient temperature. [An optimum value of the parameter a_∞ (see Figures 2 and 3) was determined using an iterative computer program in which a_∞ was allowed to vary and a linear least-squares regression analysis of the data, plotted in accordance with eq 4, was performed. The optimum value of a_∞ was taken to be that at which the regression coefficient was maximum. The same procedure was used to obtain an optimum value of the parameter a'_∞ (see Figures 4 and 5). In the latter case the experimental data were fitted using eq 6.]

Time of Desorption. Figure 4 is a plot of the total area under the VOC chromatogram in the C₆–C₁₄ region $a(t_2)$, versus the time, t_2 , for which the VOCs were desorbed from the Tenax-GC sorbent at 200 °C. Each sample was prepared using a fixed N₂ purge volume of 200 L (i.e., $t_1 = 5.46 \times 10^4$ s). It can be seen from the plot that the desorption of the bulk of the VOCs from Tenax-GC does not occur instantaneously, although ca. 21% of the adsorbed VOCs are released almost instantaneously from the sorbent when it is heated to the desorption temperature. This material is, presumably,

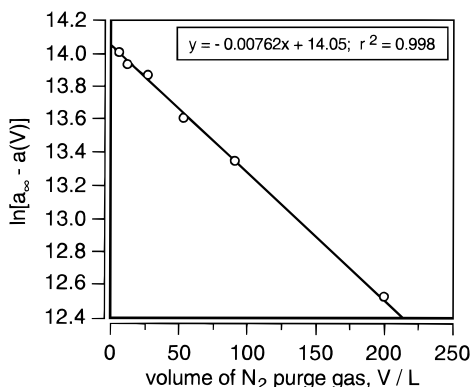


Figure 3. Plot of $\ln[a_\infty - a(V)]$ versus $V(L)$ where a_∞ is the chromatographic area obtained after the sample has been purged for an infinite time.

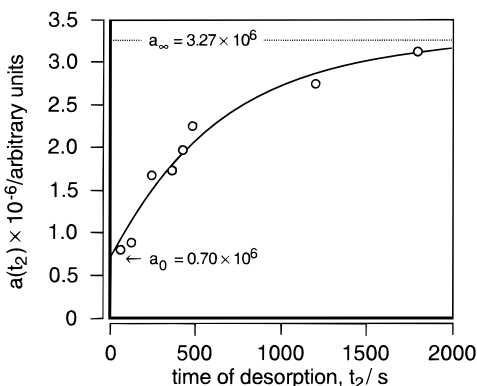


Figure 4. Plot of the total area under the VOC chromatogram in the C_6-C_{14} region, $a(t_2)$, versus t_2 , the time of desorption (s): (circles) experimental data; (solid line) computer-generated fit to the data using parameters derived from the kinetic analysis given in Figure 5. Each exposed Tenax-GC sample was prepared using 200 L of N_2 to purge 50 g of LDPE, and the VOCs were desorbed at 200 °C.

VOCs located close to the surface of the sorbent. A desorption time in excess of 1500 s is required to liberate the remaining material. This may be attributable to the latter being located more deeply within the porous sorbent. Alternatively, the VOC affinity toward the sorbent and the saturated vapor pressure of the VOC may also be involved. It may be the general case that the desorbed fraction does not have the same composition at different stages in the desorption process, and this may be of relevance when suitable desorption times are selected.

Assuming that the rate of desorption of VOCs from the sorbent is proportional to the number of moles of VOCs which remain adsorbed to it at time t_2 , eq 5 applies

$$\partial n(t_2)/\partial t_2 = k_2[n'_\infty - n(t_2)] \quad (5)$$

where $n(t_2)$ is the total number of moles of VOCs released from the sorbent at time t_2 , k_2 is a first-order rate constant for the desorption process, and n'_∞ is the number of moles of VOCs released after an infinite time of desorption. Integrating eq 5 between the time limits of zero and t_2 , and recognizing the proportionality that exists between $n(t_2)$ and the integrated GC detector response, eq 6 is obtained

$$k_2 t_2 = \ln\{(a'_\infty - a'_0)/(a'_\infty - a(t_2))\} \quad (6)$$

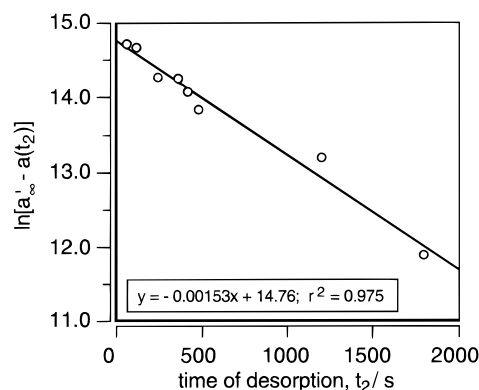


Figure 5. Plot of $\ln[a'_\infty - a(t_2)]$, where a'_∞ is the total area under the chromatogram observed after an infinite desorption time.

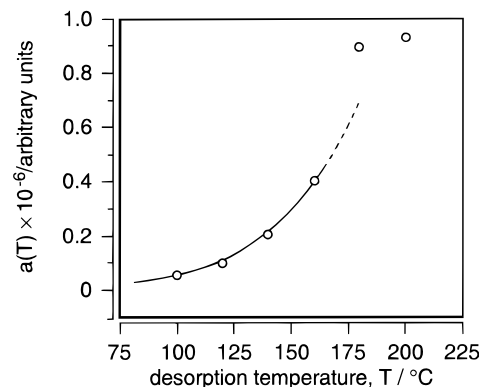


Figure 6. Plot of the total area under the VOC chromatogram in the C_6-C_{14} region, $a(T)$, versus T , the desorption temperature (°C): (circles) experimental data; (solid/broken line) computer-generated fit to the data using the thermodynamic parameters given in Table 2. Each exposed Tenax-GC sample was prepared using 200 L of N_2 to purge 50 g of LDPE, and the VOCs were desorbed for 150 s.

where a'_0 , $a(t_2)$, and a'_∞ are the integrated areas under the chromatogram obtained after desorption times $t_2 = 0$, $t_2 = t_2$, and $t_2 = \infty$, respectively. A plot of $\ln[a'_\infty - a(t_2)]$ versus t_2 is linear with a gradient $k_2 = 1.53 \times 10^{-3} \text{ s}^{-1}$ (see Figure 5).

From the kinetic analysis of the data, it is calculated that ca. 22% of the total VOCs are desorbed from the Tenax-GC sorbent and transferred to the chromatograph after a desorption period of 150 s. The data presented in Figures 4 and 5 indicate that it is possible to desorb a higher proportion of the VOCs by using a longer desorption time. Indeed, the experimental evidence suggests that no significant thermal degradation of the VOCs occurs under the desorption conditions of the experiment for desorption times as long as 1500 s. However, for convenience a desorption time of 150 s was used in the experiments reported herein and such a choice ensures that thermal degradation of the VOCs can be considered to be insignificant.

Temperature of Desorption. The relationship between the total area under the VOC chromatogram in the C_6-C_{14} region, $a(T)$, and the temperature, T , at which the VOCs are desorbed from the Tenax-GC sorbent is shown in Figure 6. In these experiments, each exposed Tenax-GC sample was prepared by purging 50 g of fresh LDPE with 200 L of N_2 and the samples were desorbed for 150 s at the particular test temperature. The desorption process is endothermic, and the data indicate that a temperature of, say, 100 °C results

Table 2. Identities and Some Thermodynamic Quantities for VOCs Isolated from LDPE at Room Temperature

peak	retention time (min)	tentative peak assignment	ΔH_i (kJ mol ⁻¹)	ΔH_{vap}^g (kJ mol ⁻¹)	C_i	r^2
1	21.29	1,2-dimethylbenzene ^a				
2	21.45	5,5-dimethyl-1-hexene	49.8	37.7 ^d	25.3	0.999
3	22.32	ethylbenzene ^a				
4	24.24	aldehyde (C ₇) ^c				
5	24.38	alkane (C ₇)	41.4	36.6 ^e	22.2	0.977
6	24.56	alcohol (C ₉) ^c				
7	25.57	octamethylcyclotetrasiloxane ^b				
8	27.26	alkene (C ₁₀)	76.6	50.5 ^e	30.3	0.851
9	27.44	alkene (C ₁₁) ^c				
10	28.15	alkene (C ₁₁)	87.1		32.7	0.864
11	28.32	2,4-dimethylheptane	33.7	42.9 ^d	20.8	0.978
12	28.54	aldehyde (C ₈)	87.5	53.7 ^f	32.8	0.982
13	30.36	aldehyde (C ₉)	52.9	58.5 ^f	23.9	0.974
14	30.50	alkane (C ₁₁)	69.5	56.3 ^e	28.4	0.940
15	31.27	decamethylcyclopentasiloxane ^b				
16	31.46	aldehyde (C ₁₂)	54.2	72.7 ^f	24.5	0.984
17	34.02	dodecane	43.8	61.3 ^d	22.0	0.980
18	35.07	alkane (C ₁₄)	42.7		21.0	0.939

^a Artifacts originating from Tenax-GC (Cao and Hewitt, 1994; Macleod and Ames, 1986). ^b Artifacts originating from chromatographic column (Hartman et al., 1993). ^c Minor peak in chromatographic window. ^d Values obtained from Wilhoit and Zwolinski (1971). ^e Consistent value given in Wilhoit and Zwolinski (1971) and in Lide (1996). ^f Values obtained from W. Steinmetz (Texas A&M University, College Station, TX, personal communication, 1997). ^g ΔH_{vap} values are those of the tentatively assigned compounds as discussed in text.

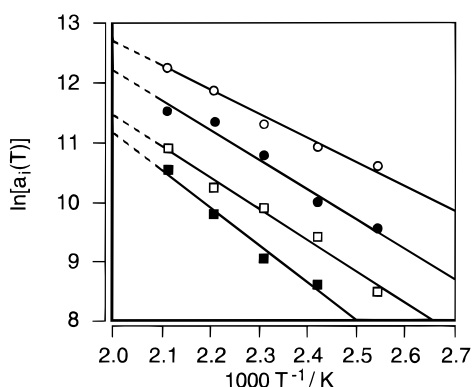


Figure 7. Plots of $\ln[a_i(T)]$ versus $1/T$ (K⁻¹) for four of the VOCs in the C₆–C₁₄ chromatographic window, where $a_i(T)$ is the peak area of an individual component: (open circles) 2,4-dimethylheptane; (solid circles) C₇ alkane; (open squares) *n*-dodecane; (solid squares) *n*-nonanal; (solid lines) linear least-squares fits to the data in accordance with the van't Hoff isochore.

only in the release of ~5% of the VOCs, which can be desorbed from the Tenax-GC sorbent in 150 s. Indeed, a desorption temperature of >180 °C is required to release most of the VOCs which are liberated in this desorption time and thereby enable the relative abundances of the components to be more accurately obtained. This finding is consistent with the work of Fales et al. (1983).

At temperatures above ca. 175 °C the values of $a(T)$ depart from the established trend, which suggests the existence of an upper asymptotic limit. The computer-generated fit of the data calculated using the thermodynamic data presented in Table 2 (see also Figure 7 and discussion below) is therefore applicable only at lower temperatures.

The effect of the desorption temperature on the intensities of the chromatographic peaks due to the individual components was also investigated in the present study. A modified form of the van't Hoff equation (see eq 7) can be readily derived for the desorption of each component, i , from the Tenax-GC substrate by (i) setting the equilibrium constant for the heterogeneous desorption of component i , K_i , equal to its vapor pressure, p_i , and (ii) recognizing the propor-

tionality that exists between the chromatographic area, $a_i(T)$, under the peak due to each component and the partial pressure of that component in the headspace. Thus

$$d \ln(K_i)/d(1/T) = d \ln(p_i)/d(1/T) \equiv d \ln[a_i(T)]/d(1/T) = -\Delta H_i/R \quad (7)$$

where ΔH_i is the enthalpy of desorption of component i , T is the thermodynamic temperature, and R is the ideal gas constant.

Figure 7 shows typical plots of $\ln[a_i(T)]$ versus $1/T$ for four of the VOCs identified in the C₆–C₁₄ chromatographic window. It was found that the temperature dependence of the peak area of the other components in this window is also fitted remarkably well by the van't Hoff isochore over the temperature range investigated. Significant deviation from this model occurs at temperatures greater than ca. 175 °C (see also Figure 6).

Table 2 lists the major components tentatively assigned in the chromatographic window along with the desorption enthalpy ΔH_i of each of these. The ΔH_i values were determined by plotting the experimentally obtained data for the peak areas in accordance with eq 7. The enthalpy of vaporization, ΔH_{vap} , of each compound is also included in Table 2 for comparison. The similarity between each desorption enthalpy and the corresponding enthalpy of vaporization suggests that the desorption process involves the volatilization of a physically adsorbed multilayer.

The total integrated area under the VOC chromatogram in the C₆–C₁₄ region, $a(T)$, at a given desorption temperature, T , can also be calculated by summing the contributions due to each component in accordance with eq 8

$$a(T) = \sum_{i=1}^n a_i(T) = \sum_{i=1}^n [C_i \exp(-\Delta H_i/RT)] \quad (8)$$

where C_i is a constant for a given compound which is determined along with ΔH_i from the van't Hoff plot of the experimental data (see Figure 7) and n is the number of compounds in the chromatographic window.

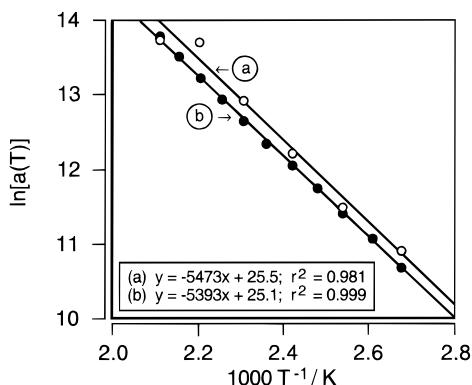


Figure 8. Plots of the natural logarithm of the total area under the VOC chromatogram in the C_6 – C_{14} region versus the desorption temperature (K): (a) (open circles) ordinate values determined by integrating each of the chromatograms; (b) (solid circles) computer-generated coordinates with ordinates calculated by summing the contribution of each of the 11 major components; (solid lines) linear least-squares regression analyses of the data sets.

Values of C_i and the linear regression coefficients, r^2 , for the fitted van't Hoff isochores are also listed in Table 2.

The experimental values of C_i and ΔH_i can be used to predict the temperature dependence of the integrated GC response. Figure 8 shows plots of $\ln[a(T)]$ versus $1/T$, where the ordinate values were determined in two different ways. The first method (see plot a) involved integrating each of the C_6 – C_{14} chromatograms obtained experimentally at the different desorption temperatures; the second method (see plot b) involved summing the expected contribution made by each major component in the chromatographic window in accordance with eq 8. The latter was achieved using a computer program to evaluate $a(T)$, and subsequently $\ln[a(T)]$, at different desorption temperatures in the range 100–200 °C. The program used C_i and ΔH_i values for the 11 most prominent peaks in the chromatographic window as indicated in Table 2.

The plots in Figure 8 are remarkably linear, indicating that the adsorption behavior of this multicomponent system may be treated, to a good approximation, as a single-component system which has an "average" desorption enthalpy of 45.5 kJ mol⁻¹. As expected, the experimentally obtained isochore lies above the theoretically generated one, and this is due to the fact that only the major chromatographic peaks were used in the construction of the latter. Furthermore, the deviation between the isochores becomes greater at higher desorption temperatures due to (i) the appearance of smaller, additional peaks in the chromatogram and (ii) the increased contribution to the area under the chromatogram made by the artifact peaks (see Table 2) which are responsible for between ca. 2% and ca. 15% of the total area at 100 and 200 °C, respectively. At 100 and 200 °C the theoretically calculated area accounts for 83.2% and 79.5%, respectively, of the total area measured experimentally. The deviation from linearity of the experimental data at high desorption temperatures is possibly due to there being very little of the VOCs remaining adsorbed to the substrate. Under these conditions the assumption of an equilibrium state is no longer valid and thus the van't Hoff equation cannot be applied to the system.

Pressure in Headspace. The effect on the total area under the VOC chromatogram in the C_6 – C_{14}

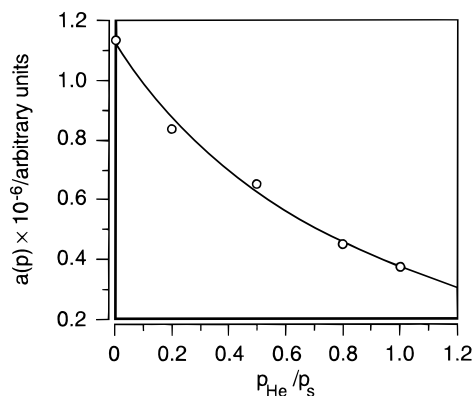


Figure 9. Plot of the total area under the VOC chromatogram in the C_6 – C_{14} region, $a(p)$, versus p_{He}/p_s , where p_{He} is the partial pressure of helium and p_s is the static pressure in the headspace vial before isothermal gas transfer: (open circles) experimental data; (solid line) computer-generated fit to the data using parameters derived from the kinetic analysis given in Figure 10. Each exposed Tenax-GC sample was prepared using 200 L of N_2 to purge 50 g of LDPE, and the VOCs were desorbed at 200 °C for 150 s.

region, $a(p)$, of adjusting the headspace pressure in the sample vial (volume V_1) with an inert gas prior to isothermally transferring the sample was examined. After each sample was desorbed for 150 s at 200 °C, the internal pressure in V_1 was adjusted using ultra-high-purity helium. Subsequently, the vapor phase was isothermally admitted to the sample loop (volume V_0) in the chromatograph. Figure 9 is a plot of $a(p)$ versus p_{He}/p_s , where p_{He} is the partial pressure of helium and p_s is the initial static pressure in V_1 . The quantity p_s is the sum of the partial pressure of each gas present initially in the sample vial prior to the addition of helium, namely air and the mixture of analyte gases. For convenience, this mixture is referred to hereafter as the "sample gas".

If p_0 and p_1 are the total pressure of the gas in V_0 and V_1 , respectively ($p_1 > p_0$ for gas transfer), and n_1 is the total number of moles of gas in V_1 initially, then the following expression can be readily derived for Δn , the total number of moles of gas transferred from V_1 to V_0 assuming ideal gas behavior:

$$\Delta n = n_1(1 - p_0/p_1)/(1 + V_1/V_0) \quad (9)$$

Since the ratio V_1/V_0 is a constant for a given chromatographic system, eq 9 can be rewritten

$$\Delta n = \theta n_1(1 - p_0/p_1) \quad (10)$$

where θ is a constant. Clearly, the number of moles of gas transferred to the sample loop is proportional to the number of moles of gas in V_1 and depends on the pressure differential across V_1 and V_0 . Thus, when a series of samples is analyzed, the initial headspace "back pressure" in V_1 should be set to the same value to ensure that a uniform quantity of gas is transferred each time to the sample loop. An inert gas, such as helium, may be used to adjust the pressure in V_1 for such purposes.

To quantitatively model the effect of adding an inert gas such as helium to V_1 , the sample gas is considered as a single component whose pressure is p_s . Although the addition of an inert gas to V_1 does not affect the position of the desorption equilibrium, it does affect the value of n_s , the number of moles of sample gas that

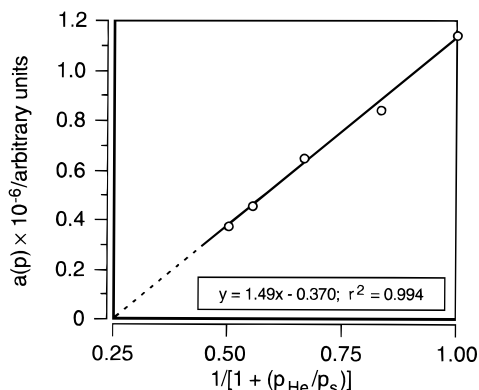


Figure 10. Plot of $a(p)$ versus $1/(1 + p_{\text{He}}/p_s)$ for the data shown in Figure 9: (open circles) experimental data; (solid line) linear least-squares regression analysis of the data.

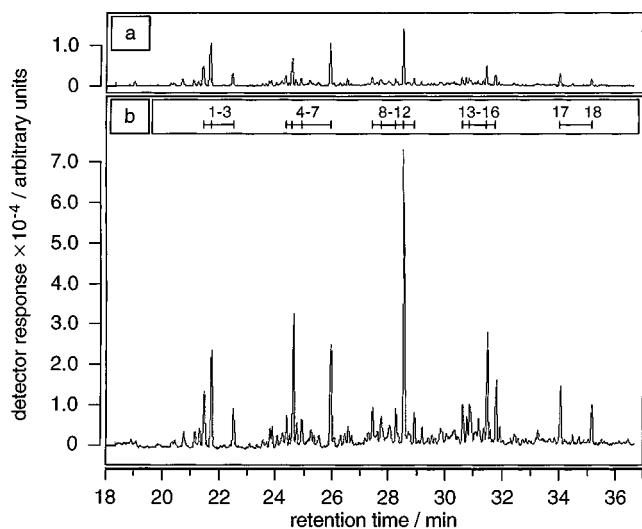


Figure 11. Chromatograms of C_6 – C_{14} VOCs in LDPE which were desorbed from Tenax-GC prepared using (a) 14.4 L of N_2 to purge 50 g of LDPE and chromatographed in accordance with typical recommendations (Fales et al., 1983) and (b) 200 L of N_2 to purge 50 g of LDPE after which the VOCs were desorbed at 200 °C for 150 s.

exists in the sample loop after isothermal transfer. In particular

$$n_s = \Delta n [p_s / (p_s + p_{\text{He}})] \quad (11)$$

where p_{He} is the partial pressure of helium in V_1 before transfer. The number of moles of analyte gas mixture in the sample loop after transfer, n_a , is proportional to n_s and, if conditions are such that Δn is constant, then the following proportionality applies:

$$n_a \propto p_s / (p_s + p_{\text{He}}) \quad (12)$$

Since the area under the chromatogram, $a(p)$, is proportional to n_a , then a plot of $a(p)$ versus $1/(1 + p_{\text{He}}/p_s)$ should be linear and exist only for abscissa values in the range zero to unity. The linearity of the plot in Figure 10 supports the above reasoning. The extrapolation of the regression line in Figure 10 to the horizontal axis produces an intercept value close to 0.25. This suggests that for $p_{\text{He}} > 3p_s$ the amount of the analyte gas mixture transferred to the sample loop is below the detection limit of the GC/MS system.

Chromatographic Analysis of LDPE. Figure 11a is a chromatogram of C_6 – C_{14} VOCs from LDPE which

were desorbed from a Tenax-GC sample, prepared using 14.4 L of N_2 to purge 50 g of LDPE, and chromatographed in accordance with typical recommendations made in the literature (Fales et al., 1983). Figure 11b shows for comparison the VOC chromatogram of the C_6 – C_{14} region of a Tenax-GC sample that was prepared using 200 L of N_2 to purge 50 g of LDPE after which the VOCs were desorbed at 200 °C for 150 s. A significant increase in the chromatographic detail is observed in Figure 11b, and this facilitates the identification of VOCs which may be responsible for deleterious organoleptic activity in LDPE.

The tentative assignment of the identities of the major chromatographic peaks (see Table 2) was achieved by searching a NIST GC/MS mass spectral library. Of the 18 peaks that are indicated, 14 can be directly attributed to VOCs derived from the LDPE. The other 4 peaks are believed to originate from either the GC column (Hartman et al., 1993) or the Tenax-GC sorbent. Indeed, aromatic artifacts originating from the thermal decomposition of Tenax-GC have been reported elsewhere (Cao and Hewitt, 1994; Macleod and Ames, 1986).

Peaks due to various C_6 – C_{12} straight-chained aldehydes were identified in the more detailed chromatogram. For instance, peaks 4, 12, 13, and 16 are believed to be due to *n*-heptanal, *n*-octanal, *n*-nonanal, and *n*-dodecanal, respectively. Such compounds are known to cause off-taste and -odor in foodstuffs exposed to them (Bigger et al., 1996). In addition to *n*-nonanol (peak 6), a series of branched and unbranched alkanes and alkenes such as 5,5-dimethyl-1-hexene (peak 2), 2,4-dimethylheptane (peak 11), and *n*-dodecane (peak 17) were also identified. Other alkanes and alkenes that were identified with a lower level of confidence include heptane (peak 5), 1-decene (peak 8), 8-methyl-1-decene (peak 9), 9-methyl-1-decene (peak 10), *n*-undecane (peak 14), and 6-methyltridecane (peak 18).

CONCLUSIONS

The results of the systematic approach developed in this paper can be used to facilitate a more satisfactory isolation and chromatographic identification of VOCs derived from LDPE at ambient temperatures. In particular, the quantitative exploration of models which adequately describe the effects of each of the experimental variables may in the future enable more reliable quantitative analyses of VOCs to be conducted via a more confident extrapolation of laboratory data. In this respect, the approach can be considered to be an advance toward optimizing the analysis of VOCs present in LDPE and has facilitated the identification of odoriphores such as C_6 – C_{14} straight-chained aldehydes, alcohols, and branched and unbranched alkanes and alkenes.

The overall rate of extraction of VOCs from LDPE using a purge gas is described adequately by first-order kinetics. A kinetic treatment of the extraction data confirms that a small, inherent level of VOCs coexists along with the solid substrate. These compounds are instantaneously extracted by the purge gas stream and are presumably responsible for any perceived odor of the material under ambient conditions. Clearly, the reliable quantification of these is of importance in assessing the organoleptic properties of the resin. Furthermore, the volumes of purge gas that have been hitherto recommended in the literature for extracting VOCs from LDPE are generally quite low and may not enable accurate quantifications of VOCs to be made.

The isothermal desorption of C₆–C₁₄ VOCs from a Tenax-GC sorbent follows first-order kinetics, and a significant proportion of these compounds is released almost instantaneously (i.e., within a few seconds after the commencement of the desorption process). The latter phenomenon may be particularly advantageous in the study of polymer systems that produce VOCs of low thermal stability, although thermal degradation of VOCs was not observed in the present study even at long desorption times. The dependence of the intensity of each chromatographic peak on the desorption temperature is described adequately by the van't Hoff isochore. The enthalpy of desorption of each component is, in general, similar in magnitude to its enthalpy of vaporization, which is consistent with the notion that each component is adsorbed physically as a multilayer on the surface of the Tenax-GC sorbent. The temperature dependence of the area under the entire chromatogram also conforms remarkably well to the van't Hoff isochore, and the experimentally observed isochore can be constructed by the summation of contributions calculated from the enthalpic data for the individual components.

The results obtained from experiments in which an inert gas is added to the headspace prior to gas transfer to the sample loop confirm that the detector response during dynamic headspace-GC analysis depends on the total pressure in the sample vial. To maximize the detector response during multiple dynamic headspace-GC analyses, isobaric conditions prior to gas transfer should be maintained and these conditions should be set in such a way that the total pressure in the sample vial is as close as practicable to the static vial pressure.

ACKNOWLEDGMENT

We thank Prof. W. Stirk Kyle, Department of Biology and Food Sciences, VUT, and Mr. Peter Thomson, Head of Science and Food Technology, TAFE, VUT, for providing technical assistance with the GC/MS system. We are grateful to Dr. R. A. Craig, Department of Physical Chemistry, University of Melbourne, for advice in relation to some of the computer modeling.

LITERATURE CITED

- Adlard, E. R.; Davenport, J. N. A study of some of the parameters in purge and trap chromatography. *Chromatographia* **1983**, *17*, 421–425.
- Al-Sammerai, D.; Al-Nidway, N. K. Polyethylene: Synthesis, properties and use. In *Handbook of Polymer Science and Technology*; Cheremisinoff, N. P., Ed.; Dekker: New York, 1989; pp 341–366.
- Anselme, C.; N'Guyen, K.; Bruchet, A.; Mallevalle, J. Can polyethylene pipes impart odors in drinking water? *Environ. Technol. Lett.* **1985**, *6*, 477–488.
- Azuma, K.; Tanaka, T.; Tsunoda, H.; Hirata, T.; Ishitani, T. Identification of the volatiles from low-density polyethylene film irradiated with an electron beam. *Agric. Biol. Chem.* **1983**, *47*, 855–860.
- Azuma, K.; Tanaka, T.; Tsunoda, H.; Hirata, T.; Ishitani, T. Effect of film variety on the amounts of carboxylic acids from electron beam irradiated polyethylene film. *Agric. Biol. Chem.* **1984**, *48*, 2003–2008.
- Bailey, W.; Liotta, C. Mechanisms of thermal degradation of polypropylene and polyethylene. *ACS Div. Polym. Chem., Polym. Prepr.* **1964**, *5*, 333–345.
- Bakker, M., Ed. *Wiley Encyclopaedia of Packaging Technology*; Wiley-Interscience: New York, 1984; p 523.
- Barabas, K.; Iring, M.; Kelen, T.; Tudos, F. Study of the thermal oxidation of polyolefins. V. Volatile products in the thermal oxidation of polyethylene. *J. Polym. Sci.* **1976**, *57*, 65–71.
- Bigger, S. W.; O'Connor, M. J.; Scheirs, J.; Janssens, J. L. G. M.; Linszen, J. P. H.; Legger-Huysman, A. Odour characterization of low-density polyethylene used for food-contact applications. In *Polymer Durability: Degradation, Stabilization and Lifetime Prediction*; ACS Advances in Chemistry Series 249; American Chemical Society: Washington, DC, 1996; pp 249–268.
- Bravo, A.; Hotchkiss, J. H. Identification of volatile compounds resulting from the thermal oxidation of polyethylene. *J. Appl. Polym. Sci.* **1993**, *47*, 1741–1748.
- Bravo, A.; Hotchkiss, J. H.; Acree, T. E. Identification of odorous compounds resulting from the thermal oxidation of polyethylene. *J. Agric. Food Chem.* **1992**, *40*, 1881–1885.
- Cao, X-L.; Hewitt, C. N. Build-up of artifacts on adsorbents during storage and its effect on passive sampling and gas chromatography-flame ionization detection of low concentrations of volatile organic compounds in air. *J. Chromatogr.* **1994**, *688*, 368–374.
- Chuang, C. R. Analysis of odour problems in polyolefin packaging materials. *SPE J.* **1984**, 246–247.
- Culter, J. D. Minimizing plastic package/product interactions—An unfilled need. *J. Plast. Film Sheet.* **1992**, *8*, 208–226.
- Dalbey, W. E.; Bynum, L. M.; Mooney, J. K.; Pulkowski, C. H. Sensory irritation in mice during exposure to thermal decomposition products of polyethylene. *ANTEC Proc.* **1992**, 92–93.
- Eiceman, G. A.; Karasek, F. W. Identification of residual organic compounds in food packages. *J. Chromatogr.* **1981**, *210*, 93–103.
- Fales, N. J.; Stover, L. C.; Lamm, J. D. A methodology for testing polymer odor and odor contributors. *Polym. Plast. Technol. Eng.* **1983**, *21*, 111–128.
- Forrest, M. J.; Jolly, A. M.; Holding, S. R.; Richards, S. J. Emissions from processing thermoplastics. *Ann. Occup. Hyg.* **1995**, *39*, 35–53.
- Gramshaw, J. W.; Vandenburg, H. J.; Lakin, R. A. Identification of potential migrants from samples of dual-ovenable plastics. *Food Addit. Contam.* **1995**, *12*, 211–222.
- Grassie, N.; Scott, G. In *Polymer Degradation and Stabilization*; Cambridge University Press: New York, 1985.
- Hagman, A.; Jacobsson, S. Theoretical model for quantitative determination of volatile compounds in polymers by dynamic headspace sampling. *Anal. Chem.* **1989**, *61*, 1202–1207.
- Hartman, T. G.; Lech, J.; Karmas, K.; Salinas, J.; Rosan, R. T.; Ho, C-T. Flavor characterization using adsorbent trapping-thermal desorption-gas chromatography and gas chromatography-mass spectrometry. In *Flavor Measurement*; Dekker: New York, 1993; pp 37–60.
- Hayashi, H.; Matsuzawa, S. Vaporization behaviour of antioxidant additive BHT in polypropylene by heating. *J. Appl. Polym. Sci.* **1993**, *49*, 1825–1833.
- Hoff, A.; Jacobsson, S. Thermooxidative degradation of low-density polyethylene close to industrial processing conditions. *J. Appl. Polym. Sci.* **1981**, *26*, 3409–3423.
- Hoff, A.; Jacobsson, S.; Pfaffli, P.; Zitting, A.; Frostling, A. Degradation products of plastics. *Scand. J. Work Environ. Health* **1982**, *8* (Suppl. 2), 1–60.
- Kaljurand, M.; Smit, H. C. Comparison of sample concentration methods and correlation chromatography for polymer dynamic headspace studies. *Chromatographia* **1994**, *39*, 210–215.
- Kim, H.; Gilbert, S. G. Thermally generated volatile compounds in packaging materials. In *Thermal Generation of Aromas*; ACS Symposium Series 409; American Chemical Society: Washington, DC, 1989; pp 396–404.
- Kim-Kang, H. Volatiles in packaging materials. *Crit. Rev. Food. Sci. Nutr.* **1990**, *29*, 255–271.
- Kiselkev, A. V.; Maltsev, V. V.; Saada, B.; Valovoy, V. A. Gas chromatography-mass-spectrometry of volatiles released

- from plastics used as building materials. *Chromatographia* **1983**, *10*, 539–544.
- Kolb, B.; Pospisil, P.; Auer, M. Quantitative headspace analysis of solid samples; a classification of various sample types. *Chromatographia* **1984**, *19*, 113–122.
- Kozinowski, J.; Piringer, O. Evaluation of off-odours in food packaging—The role of conjugated unsaturated carbonyl compounds. *J. Plast. Film. Sheet.* **1986**, *2*, 40–50.
- Lide, D. R., Ed. In *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL, 1996.
- Linssen, J. P. H.; Janssens, J. L. G. M.; Roozen, J. P.; Posthumus, M. A. Sensory descriptors for a taint in water packed in test pouches made of polyethylene lined aluminium. *J. Plast. Film Sheet.* **1991**, *7*, 294–305.
- Linssen, J. P. H.; Janssens, J. L. G. M.; Roozen, J. P.; Posthumus, M. A. Combined gas chromatography and sniffing port analysis of volatile compounds of mineral water packed in polyethylene laminated packages. *Food Chem.* **1993**, *46*, 367–371.
- Long, J. W.; Snyder, R. W.; Spalik, J. Purge-and-trap gas chromatographic method for residual volatiles in high temperature polymers. *J. Chromatogr.* **1988**, *450*, 394–398.
- Macleod, G.; Ames, J. M., Comparative assessment of the artefact background on thermal desorption of Tenax GC and Tenax TA. *J. Chromatogr.* **1986**, *355*, 393–398.
- McGorin, R. J.; Pofahl, T. R.; Croasmun, W. R. Identification of the musty component from an off-odor packaging film. *Anal. Chem.* **1987**, *59*, 1109A–1112A.
- Nielson, R. C. Supercritical fluid extraction coupled with gas chromatography for the analysis of aroma compounds adsorbed by low-density polyethylene. *J. Liq. Chrom.* **1991**, *39*, 1234–1237.
- Novotny, M.; Lee, M. L.; Bartle, K. D. Some Analytical aspects of the chromatographic headspace concentration method using a porous polymer. *Chromatographia* **1974**, *7*, 333–338.
- Peled, R.; Mannheim, C. H. Off-flavors from packaging materials. *Mod. Packag.* **1977**, *50*, 45–65.
- Sakodynskii, K.; Panina, L.; Klinskaya, N. A study of some properties of Tenax, a porous polymer sorbent. *Chromatographia* **1974**, *7*, 339–344.
- Tou, J. C.; Rulf, D. C.; De Lassus, P. T. Mass spectrometric system for the measurement of aroma/flavor permeation rates across polymer films. *Anal. Chem.* **1990**, *62*, 592–597.
- Van Wijk, R. The use of poly-*p*-2,6-diphenylphenylene oxide as a porous polymer in gas chromatography. *J. Chromatogr. Sci.* **1970**, *8*, 418–420.
- Wilhoit, R. C.; Zwolinski, B. J. In *Handbook of Vapour Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds*; Thermodynamics Research Center, Department of Chemistry, Austin, TX, 1971.
- Zlatkis, A.; Lichtenstein, H. A.; Tishbee, A. Concentration and analysis of trace volatile organics in gases and biological fluids with a new solid adsorbent. *Chromatographia* **1973**, *6*, 67–70.

Received for review August 18, 1997. Revised manuscript received December 4, 1997. Accepted December 11, 1997. We are grateful to Kemcor Australia Limited, ARC Small Grants Scheme, and the Centre for Packaging, Transportation and Storage, Victoria University of Technology, for financial support.

JF970717E