

Interactions between Reactive Aroma Compounds from Model Citrus Juice with Polypropylene Packaging Film

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Polypropylene film for food packaging was immersed into an acidic model solution containing 10 aroma compounds (e.g. pinenes, limonene, citrals). Sorption was determined by the use of two complementary methods: solvent extraction and multiple headspace extraction. A complete mass balance of the aroma compounds considering their reactivities in acidic condition was established. It appears that sorption protects the most reactive terpenes from degradation and thus minimizes the formation of compounds which could behave as off-flavors (e.g. α -terpineol). The consequences of this reactivity on the evaluation of the partition coefficient of aroma between juice and packaging are discussed.

Keywords: Sorption; aroma compounds; multiple headspace extraction; partition coefficients; polypropylene

INTRODUCTION

Plastic materials have many advantages with regard to food packaging. However, they can also interact with foodstuffs, giving rise to sorption of food constituents, among other physicochemical events. The sorption of fats (Arora and Halek, 1994; Johansson and Leufvén, 1995) and of aroma compounds (Leufvén and Hermansson, 1994; Giacin, 1995) affects the quality of packaged food. Fat sorption may enhance both migration of polymer additives into food (Vom Bruck *et al.*, 1981) and penetration of food constituents into the package. Aroma sorption may be large enough to affect the organoleptic quality of packaged food. Food industries must therefore often correct this sorption effect and add excess amounts of flavors to the food for the taste and flavor to be still acceptable for consumers until the end of the product's shelf life.

Furthermore, since aromas are complex mixtures, sorption may be selective, leading to changes in the organoleptic profile of foods. This selectivity depends on the type of food. With solid food, where the contact with the package often occurs through a small gas phase, aroma losses largely depend both on the vapor pressure and on the solubility of active constituents in the polymer (Halek, 1988). With aqueous foods (e.g. juices), the relevant parameters are the partition coefficient of aroma compounds between packaging and food (Kwapong and Hotchkiss, 1987; Shimoda *et al.*, 1988; Imai *et al.*, 1990; Nielsen *et al.*, 1992a,b). Sorbed aromas may permeate through the material, and evaporate outside the package, at a rate that depends both on their diffusivity and on their solubility in the polymer.

Most of the work in the literature has focused on the weight uptake sorption phenomenon, usually by monitoring the decrease in the concentration of aromas in

the solution over time (Moshonas and Shaw, 1989; Dürr *et al.*, 1981; Paik and Venables, 1991; Konzcal *et al.*, 1992). However, aroma constituents of citrus juice are often fragile molecules, vulnerable to chemical degradation either through oxidation or through acid catalysis mechanisms (Anandaraman and Reineccius, 1986; Marsili, 1986; Clark and Chamblee, 1992; Saleeb and Ikenberry, 1993; Kutty *et al.*, 1994). Much of the work has been carried out at high concentrations of aroma compounds, with addition of emulsifier or ethanol to increase the solubility of the lipophilic compounds. This facilitates analytical work but might modify unrealistically the studied phenomena. The partition between packaging and food may be affected by the presence of a third phase, namely excess aroma. Analytical approaches are needed to provide a complete view of all the phenomena occurring during shelf life. The purpose of this work is to evaluate and optimize analytical methods to account for all of the phenomena occurring between a model fruit juice and its polypropylene packaging material.

MATERIALS AND METHODS

Materials. The polymer packaging material used was a semicrystalline ethylene–polypropylene copolymer (PP) (thickness = 40 μm , $d = 1.018$, Elf Atochem, Serquigny, France). Analytical grade aroma compounds were studied: α -pinene, β -pinene (Fluka, St. Quentin Fallavier, France), myrcene (Interchim, Paris, France), d-limonene, octanal, decanal, ethyl 2-methylbutyrate (E2MB), nonan-2-one, α -terpineol, and citral (Aldrich, Strasbourg, France). Citric acid and sodium citrate were obtained from Prolabo (Fontenay s/Bois, France). Solutions were made up with ultrapure water, obtained from a Milli-Q system (Millipore, Bedford, MA). Hexane (Prolabo) and HPLC grade pentane (Fisons, Arcueil, France) used were distilled to get the proper gas chromatography purity. Paraffin oil (Almo, St. Genis Laval, France) was used as a solvent for standards in the headspace technique.

Sample Preparation. All solutions of the aroma compounds were prepared using a citrate buffer (0.976 g/L citric acid and 0.103 g/L sodium citrate in ultrapure water) as solvent. pH 3.0 was controlled and monitored using a pH-meter (Model 605, Metrohm, Roucaire, France). Sodium azide (Aldrich, 0.02% w/w) was added to prevent microbacterial changes during storage.

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The model solution containing all of the aroma compounds (5–12 $\mu\text{L/L}$) was prepared in citrate buffer at 4 °C. The pure aroma compounds were introduced using a micropipet equipped with a glass capillary tube (Transfertector, Brand, Paris). To evaluate their stability, solutions of each aroma compound (control samples 1) were prepared using the same procedure. The solutions were homogenized by an ultrasonic treatment (Model TK52, Labo-Moderne, Paris, France) for 20 min after preparation.

Contact Conditions. Experimental samples were prepared by immersing strips of PP film (13 × 13 cm) into 266 mL glass flasks filled with the model solution and tightly stoppered with Teflon caps. Experimental samples and model solution without film (control sample 2) were stored at 18 ± 1 °C in a dark room. After different contact times (1, 3, 6, 14 days), experimental samples (two samples for each time) and control sample 2 (one sample) were analyzed according to two different extraction methods: solvent extraction and headspace analysis.

Solvent Extraction. At each contact time, film and solution from experimental samples were separated and extracted by solvent in a room at 4 °C, using tightly stoppered glass flasks to prevent losses of volatiles. Pentane (bp = 36 °C) and hexane (bp = 69 °C) were tested as extraction solvents. Concentration of the hexane solution using a Kuderna-Danish apparatus (Ferreira *et al.*, 1995) required a higher distillation temperature and led to losses of the volatile compounds during the concentration step as compared to pentane.

The solution (issued of experimental sample, control samples 1, and control sample 2) (100 mL) was extracted three times with pentane (20 mL) in a 150 mL flask to limit losses of volatiles in the headspace above the solution. One milliliter of a solution of myrcene and nonan-2-one in pentane (800 $\mu\text{L/L}$) was added as internal standard. Collected extracts were dried with sodium sulfate and filtered on glass wool.

The film was removed from experimental samples, carefully rinsed and wiped, separated in two parts, and then immediately plunged into a 100 mL flask containing pentane (80 mL). One milliliter of a solution of myrcene and nonan-2-one in pentane (800 $\mu\text{L/L}$) was added. Extraction was carried out for 2 h, alternating magnetic stirring and ultrasonic treatment (US) periods (15 min each), to limit pentane warmup and excess pressure in the flask during US. US of a solution of aroma compounds (10 $\mu\text{L/L}$) in hexane for periods up to 1 h showed that this step did not induce any chemical degradation. The efficiency of extraction of the solution and of the film was checked with a further extraction by dichloromethane. No significant amount of aroma compound was detected in the latter extraction.

Multiple Headspace Extraction (MHE) Using a Purge and Trap Injector (PTI). An automatic PTI (Chrompack, Les Ulis, France) coupled to a gas chromatograph (GC) was used for dynamic MHE of the volatile compounds from both aqueous solutions and films. The PTI apparatus has been described elsewhere (Ehret-Henry *et al.*, 1993). The instrument consists of three parts: a purge cell containing the sample (film or solution) to be analysed, a cryogenic trap where volatiles are focused, and a GC whose injector is coupled to the trap. A flow of purge gas (helium, also the carrier gas) passed through the purge cell and swept the volatiles into a cryogenic trap (0.53 mm × 15 cm; CP-Sil 5 DB) held at -120 °C with liquid nitrogen. After the purge time, trapped volatiles were thermally flash desorbed and directly injected in the GC column. With aqueous samples a water condenser at -10 °C is used between the purge cell and the cryogenic trap to prevent blocking of the latter by ice crystals. The whole procedure was automatically controlled and repeated for MHE through an injector control unit.

The sample solution (1 mL) and ultrapure water (ca. 3 mL previously saturated with helium) (Ehret-Henry *et al.*, 1993; Le Sech *et al.*, 1994) were introduced into the purge cell. A solution of myrcene in water (1 mL, 5 $\mu\text{L/L}$) was added as internal standard. Due to its low solubility in water (10.3 mg/L) (Lebossé *et al.*, 1996), myrcene solution was prepared in a 1 L flask and homogenized with magnetic stirring for 30 min before use. Equilibration time and temperature were reported

to be the major parameters for the MHE desorption profiles (Kolb and Ettre, 1991). Thirty minutes of equilibration time was applied before the first purge. Temperature was fixed at 40 °C. Repeated headspace extraction enabled a complete desorption of volatiles after three purge cycles of 10 min.

The film (5 cm²) was placed into the purge cell with 10 μL of a solution of myrcene and nonan-2-one (800 $\mu\text{L/L}$) in paraffin oil (internal standards). Paraffin oil was devolatilized for 1 h at 120 °C with nitrogen gas prior use. Film was analyzed with four purge cycles of 5 min at 60 °C.

GC. GC analysis of solvent extracts of solutions and films was performed using a Carlo Erba Model HRGC-5160 Mega Series (Fisons) with an on-column injector and a FID detector. Separation was achieved with a DB-Wax fused silica capillary column (0.32 mm × 30 m and 0.5 μm film thickness, J&W Folsom, CA) with a 3 m deactivated precolumn. Hydrogen was used as carrier gas (flow rate = 4.4 mL/min at 40 °C). Injector port was cooled by an ambient air flow during sampling. Detector was heated to 250 °C. A linear temperature program (6 °C/min) was run up to 220 °C after 4 min at 40 °C. FID was connected to a Shimadzu (Touzart & Matignon, Vitry/Seine, France) Model C-R5A integrator, and signal was treated with a chromatographic acquisition software (Borwin version 1.2, JMBS Developpements, Le Fontanil, France) for quantification.

Headspace analysis was achieved with a Carlo Erba chromatograph Model 4160 Fractovap with a FID detector connected to a SP4270 integrator (ThermoSeparation Products, Les Ulis, France). A DB-Wax fused silica capillary column (0.32 mm × 30 m, 0.5 μm thickness, J&W) was used for separation with helium as carrier gas (flow rate = 4.5 mL/min at 40 °C). Oven temperature was programmed from 40 to 160 °C at a rate of 3 °C/min and was further increased to 200 °C at a rate of 6 °C/min. The signal was treated as described above.

The GC/MS system consists of a Fisons GC-8000 chromatograph and an MD-800 mass spectrometer (Fisons Instruments). Separations were performed on a Supelcowax fused silica capillary column (0.32 mm × 30 m; 0.5 μm ; Supelco, Bellefonte, PA). Helium was at 2 mL/min. Oven temperature was programmed from 40 to 160 °C at a rate of 3 °C/min and was further increased to 200 °C at a rate of 6 °C/min. Electron impact mass spectra were recorded with the following conditions: capillary direct interface, 250 °C; ion source, 200 °C; ionization voltage, 70 eV; mass range, 35–300 m/z ; electron multiplier voltage, 360 V; scan rate, 3 scans/s. Spectra were treated with MassLab software (Fisons) and compared with spectra of the NIST library.

RESULTS AND DISCUSSIONS

Solubility of the Aroma Compounds. The aroma compounds studied here (Table 1) are typical of citrus juice composition (Radford *et al.*, 1974; Dürr *et al.*, 1981; Moshonas and Shaw, 1986; Nisperos-Carriedo and Shaw, 1990) and exhibit a broad range of chemical structures. Due to the importance of the phase equilibrium in the interaction, it was essential to have only a biphasic system: the plastic and the solution with exclusion of excess aroma. The solubility of aroma compounds in water was determined by a GC method involving a direct injection of aqueous solutions (Lebossé *et al.*, 1996). Their concentration in the model solution was always below saturation. Compared to pure water, the presence of citric acid based buffer (pH 3) caused a decrease of the solubility, especially for the weakly soluble hydrocarbons (limonene, α -pinene, β -pinene). Solubilities of the aroma compounds, their concentrations in the model solution, and their characteristics are listed in Table 1.

Choice of the Analytical Methods. Since any analytical procedure may lead to losses of volatiles, we decided to use two different procedures: solvent extrac-

Table 1. Characteristics of the Aroma Compounds Used in the Citrus Juice Model Solution

no.	aroma compound	Kovats index ^c	bp (°C)	solubility ^b (mg L ⁻¹)	concn (mg L ⁻¹)	M _w	FID response	purity ^f (%)
1	α-pinene	1023	156	4.8	4.3	136	0.86 ^d	99.8
2	ethyl 2-methylbutyrate	1066	132	1990	10.4	130	1.40 ^d	99.3
3	β-pinene	1122	165	12.0	4.2	136	0.83 ^d	96.8
4	limonene	1204	178	9.5	4.2	136	0.83 ^d	99.7
5	octanal	1312	171	242	6.1	128	1.25 ^d	92.8
6	decanal	1515	208	15.6	9.8	156	0.97 ^e	98.3
7	linalol	1563	199		9.7	154	0.88 ^e	98.0
8	citral ^g /neral	1692	229	241	6.2	152	0.79 ^e	99.5
9	α-terpineol	1718	220		11.3	154	0.73 ^e	98.9
10	citral ^g /geranial	1746	229	289	11.1	152	0.81 ^e	99.5

^a The respective proportions of geranial and neral (measured by GC) are 35.5% and 64.5%. ^b See Lebossé *et al.* (1996). ^c Measured with DB-Wax column. ^d Relative response to myrcene standard. ^e Relative response to nonan-2-one standard. ^f Measured by GC.

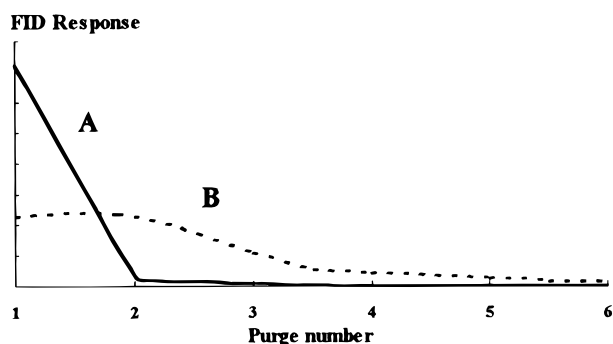


Figure 1. MHE profiles for high-volatility compounds (A) and lower volatility compounds (B) from aqueous solution (purge cell temperature, 23 °C; purge time, 10 min; equilibration time before the first purge, 10 min; analytical time between each measure, 50 min).

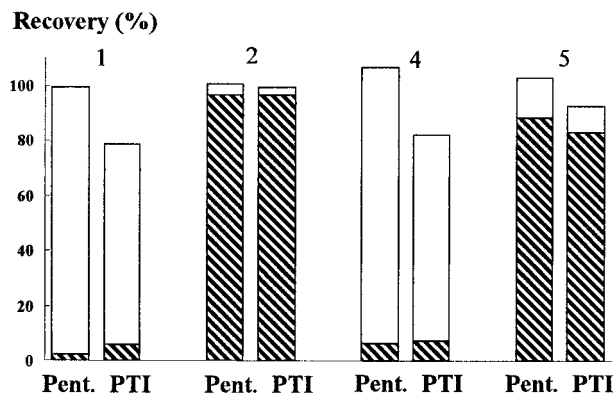


Figure 2. Comparison of both extraction methods (pentane extraction and MHE-PTI procedure): recovery (percent) of α-pinene (1), E2MB (2), limonene (4), and octanal (5) from PP film (white bar) and from solution (slashed bar) after 1 day of contact. Mean of two determinations is shown for each method.

tion and MHE-PTI. Since they are based on different physical properties, each one should validate the results obtained with the other one. Using MHE-PTI, two typical desorption profiles were obtained from solutions or films. The most volatile compounds (pinenes, limonene) were almost completely extracted after one purge (desorption profile A, Figure 1). With the less volatile aroma compounds, the decrease was much lower, and the second purge was often more efficient than the first one (desorption profile B, Figure 1). We therefore used two internal standards dissolved in paraffin oil: myrcene for the most volatile compounds and nonan-2-one for the higher molecular weight compounds.

Figure 2 shows the percentage of recovery for representative aroma compounds using both methods after 1 day of contact with PP film. Solvent and MHE-PTI extractions for solutions gave consistent results up to

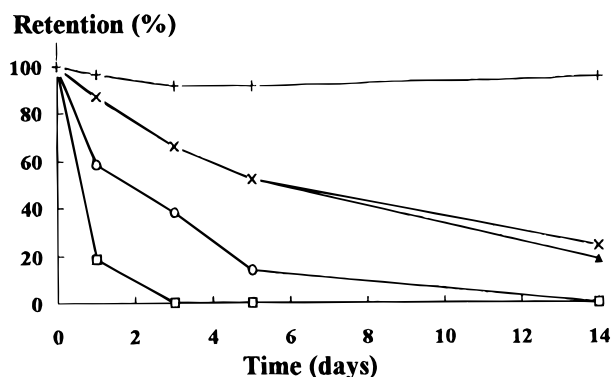


Figure 3. Retention (percent) of β-pinene (□), α-pinene (○), neral (▲), and geranial (×) during storage of the acidic model solution. Linalol (+) is also given for comparison (average of two extractions by pentane).

octanal. Compounds with molecular weight higher than that of octanal were trapped by the condenser and could not be analyzed with PTI. This strongly limited the scope of volatile compounds analyzed using the PTI procedure. For films, MHE-PTI led to a slight systematic underestimation of the results, probably due to low differences in desorption between film and paraffin. Both methods thus appear to be very complementary: solvent extraction gives good results but is highly tedious and time-consuming; on the other hand, MHE-PTI is more convenient and can be fully automated, but it is best for the most volatile aroma compounds.

Analysis of PP Film before Contact. Polyolefin films naturally contain volatile compounds. These volatile compounds were easily detected by MHE-PTI analysis. To avoid interferences with the sorbed aroma constituents, the volatile compounds of the PP films were carefully removed at 40 °C in an air oven for 24 h before use. A higher temperature (70 °C) led to the generation of new volatiles, probably through well-known oxidation processes (Bernard, 1991; Boone *et al.*, 1993; Bravo and Hotchkiss, 1993; Vaillant *et al.*, 1994; Marqué, 1995).

Analysis of Control Samples 1 and 2. Before studying sorption experiments, we needed to have knowledge about the reactivity of aroma compounds in acidic solution. Results obtained from the extraction of control sample 2 are shown in Figure 3. After 3 days, most of the β-pinene and 60% of α-pinene are lost. Neral and geranial were slightly more stable, exhibiting 60% of degradation after 14 days. Other aroma compounds (E2MB, octanal, limonene, decanal, linalol) were quite stable during the experimental time.

After 14 days, GC/MS analysis of control samples 1 (individual compounds without film) showed numerous degradation products. Identified reaction products of

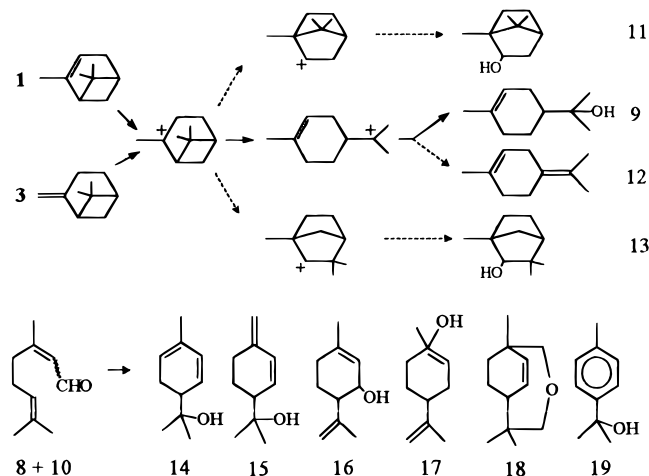


Figure 4. Rearrangement of α - and β -pinenes and citrals in acidic solution (1, α -pinene; 3, β -pinene; 8, neral; 9, α -terpineol; 10, geranial; 11, α -fenchol; 12, terpinolene; 13, borneol; 14–17, menthadienols; 18, dehydrocineol; 19, *p*-cymenol).

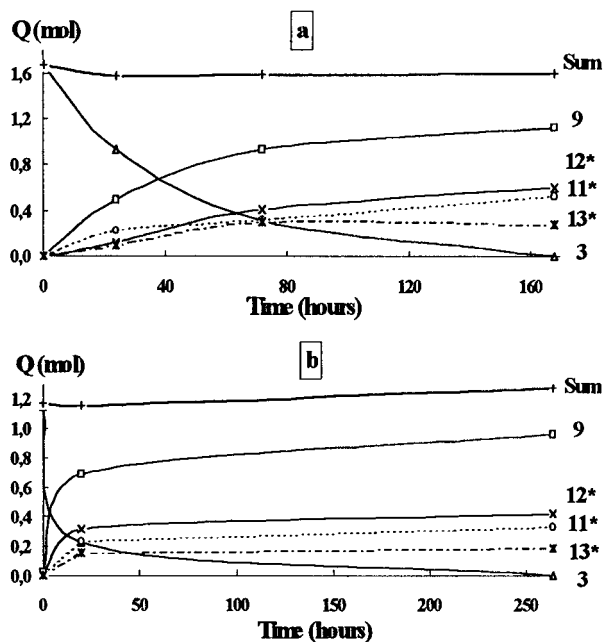


Figure 5. Evolution of molar quantities (Q) of α -pinene (a) and β -pinene (b) versus time (symbols as in Figure 4). *For a better representation of degradation compounds 11–13, y -scale was magnified by a factor 3.

α -pinene and β -pinene (through retention indexes and mass spectra) were α -terpineol (9), borneol (11), terpinolene (12), and α -fenchol (13), in agreement with the literature (Clark and Chamblee, 1992) (Figure 4). At any time, the sum of peak areas of pinenes and of their four reaction products corresponded to the initial area of pinenes (Figure 5).

In our experimental conditions, little degradation of limonene was observed; α -terpineol represents only 8.8% of the initial quantity of limonene. This result parallels those reported by several authors (Buckholz and Daun, 1978; Rodriguez *et al.*, 1991; Saleeb and Ikenberry, 1993), who concluded that formation of α -terpineol in limonene solution is a slow process. In orange juice, α -terpineol is the major off-odor compound for long-term storage, and its main precursor was assumed to be limonene (Dürr *et al.*, 1981; Moshonas and Shaw, 1989). It has been suggested on the basis of Charm values that absorption of limonene by container plastics is unlikely to impact the aroma of orange juice directly (Marin *et*

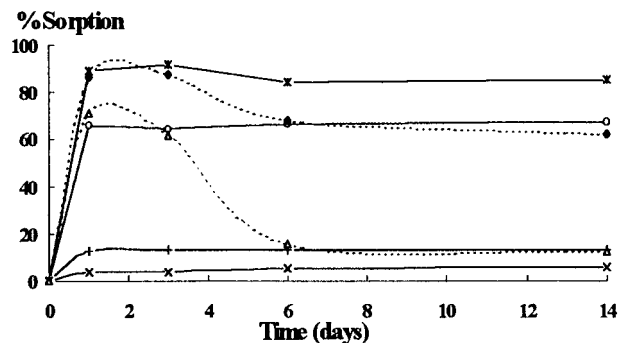


Figure 6. Sorptions of limonene (*), α -pinene (\blacklozenge), β -pinene (\blacktriangle), decanal (\circ), octanal (+), and E2MB (\times) in PP film during storage. Sorptions of neral, geranial, and linalol accounting for <5% are not represented.

al., 1992). Its loss by sorption may minimize the formation of off-aromas such as α -terpineol.

Stored under the same conditions, geranial and neral gave a complex chromatographic profile with no major reaction product. GC/MS analysis suggested the presence of products 14–19 (Figure 4). The mass balance was not complete in this case. The total quantity of the many reaction products detected in our GC conditions accounted together with residual citrals for <32% of the initial quantity. The reactivity of these aldehydes has been recently rationalized (Saleeb and Ikenberry, 1993; Clark and Chamblee, 1992; Richard *et al.*, 1995). The major reaction products cited are diols, which are not eluted in the GC conditions used here.

Kinetics of Sorption into PP Film. Kinetics of sorption in film monitored by solvent extraction procedures are shown in Figure 6. These results were validated by MHE–PTI analysis (results not displayed here). For all compounds, maximum sorption was observed after 1 day of contact. In a first approximation, observed differences in sorption follow the differences in solubility (Table 1). Sorption by PP at 1 day follows the inverse order of polarity, according to the rule that “like dissolves like”: pinenes, limonene > decanal > octanal > E2MB. A similar trend was reported for polyethylene, where dodecanal is sorbed to a greater extent than decanal (Charara *et al.*, 1992). The chain length of the lipophilic portion appeared to affect the sorption of aldehydes into polyolefins.

For longer contact times, others factors appear for reactive compounds. Figure 7 compares GC/MS chromatograms of the extracts from both film and solution after 14 days of contact, in comparison with initial model solution. The apolar reaction product 12 (terpinolene) is sorbed in the film (Figure 7b) while other polar reaction products (11, 13, 14–19) remain in the solution (Figure 7c).

To facilitate an overview of the results, we have superimposed on Figure 8 the mass balance for each compound in the absence and presence of PP film (film + solution). As α -terpineol has been found to be the major reaction product of pinenes, its complete mass balance was not established. Two distinct behaviors appear on the basis of the stability of aroma compounds in the absence and presence of film.

Compounds Whose Degradation Is Influenced by the Film. α -Pinene and β -pinene, which are highly reactive in acidic solution, are found to be sorbed into PP film to a large extent. Without film, these compounds would disappear by degradation. Even if they are not available for consumers, since they are totally located in the film, the presence of the film prevents or reduces the

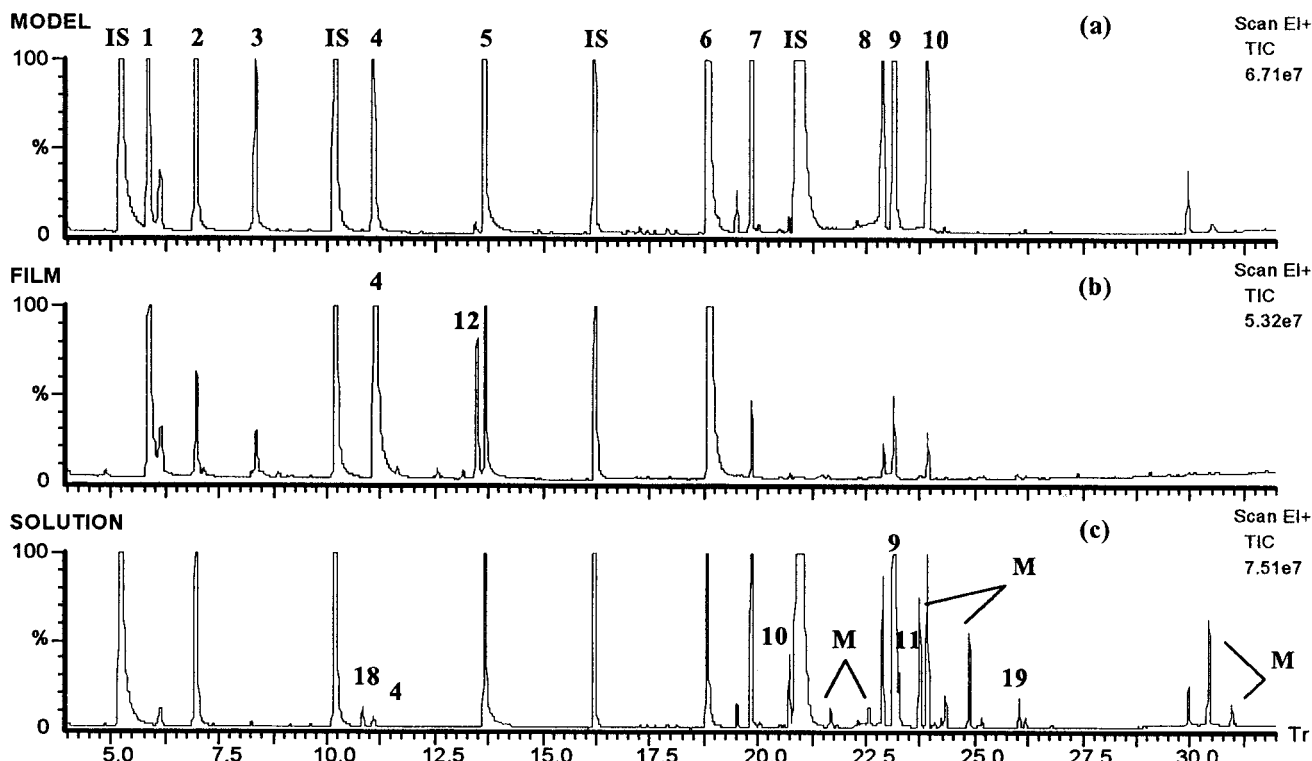


Figure 7. GC/MS chromatograms of the solvent extracts from model solution (a), film (b), and solution after immersion (c), after 14 days of contact (symbols as in Figure 4; M, menthadienols 14–17).

Recovery (%)

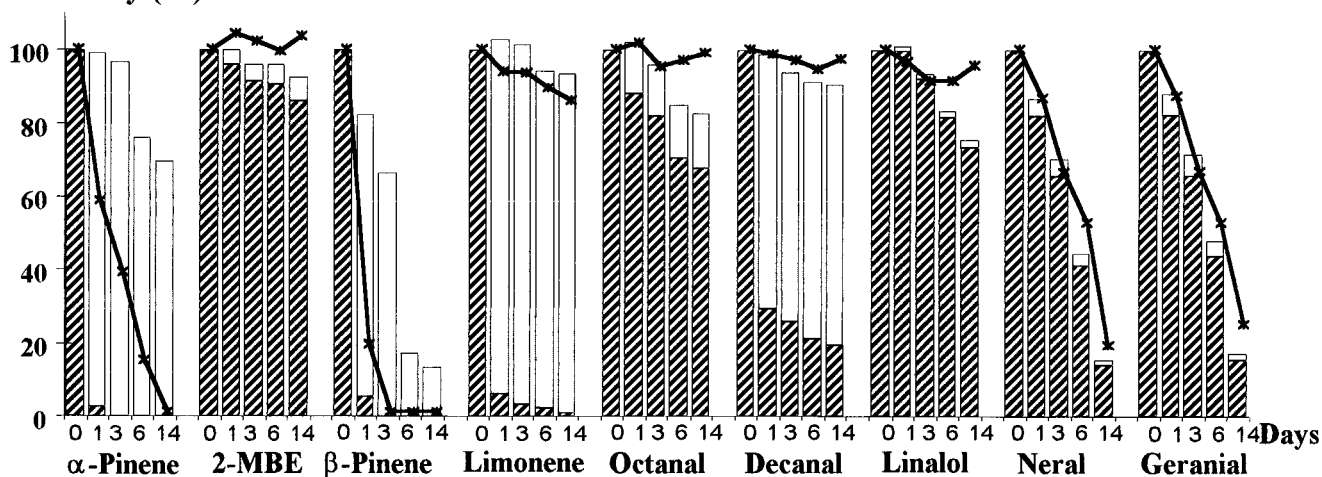


Figure 8. Recovered aroma compounds (percent) from the solution (slashed bar) and from PP film (white bar) at 1, 3, 6, and 14 days of contact: comparison with model solution alone (x).

formation of reaction products **9** and **11–13**. Compound **9** (α -terpineol) has been reported as an undesirable off-flavor in citrus oils, contributing to a stale and musty aroma in orange juice (Tatum *et al.*, 1975; Rodriguez *et al.*, 1991).

Compounds Whose Degradation Is Not Influenced by PP Film. Limonene and citrals are not influenced by PP film. Little sorption of geranial and neral into PP was apparently detected. This result corresponded to findings of Charara *et al.* (1992) for PE. In fact, these compounds have a behavior that closely parallels their reactivity in solution in the absence of film.

Sorption of fruit juice aroma compounds in contact with plastic packaging is usually governed by their partition coefficient (K) between solution and polymer. K needs to be accurately measured. Depending on analytical approach, there are two ways to measure K .

The most convenient way is to measure the concentration in the solution at equilibrium (C_{sol}). K_1 is then obtained from

$$K_1 = \frac{(Q_0 - Q_t)/V_{film}}{C_{sol}} \quad (1)$$

where Q_0 and Q_t are, respectively, the quantity (mg) of compound in the initial solution ($t = 0$) and in the solution after contact (t) and V_{film} is the volume of the film (dm^3). The tedious way to determine K is to extract volatiles from polymer and measure C_{film} . K_2 is then obtained from

$$K_2 = C_{film}/C_{sol} \quad (2)$$

C_{film} and C_{sol} are the concentrations (mg/L) into the film

Table 2. Partition Coefficients after 14 Days of Contact, Determined from Equations 1 and 2

aroma compound	K_1	K_2
α -pinene	<i>a</i>	<i>a</i>
E2MB	64	31
β -pinene	<i>a</i>	<i>a</i>
limonene	42 300	40 800
octanal	186	87
decanal	1 630	1 490
linalol	142	11
neral	2 410	42
geranial	2 150	46

^a $C_{sol} = 0$.

and the solution, respectively, at equilibrium. Partition coefficients K_1 and K_2 at 14 days, when the steady state is reached; are compared in Table 2. For stable compounds eqs 1 and 2 are expected to yield equivalent results, as we found for limonene and decanal. For unstable compounds such as neral and geranial $K_1 \gg K_2$; the affinity of these molecules for the tested polymer is overestimated.

Conclusion. Absorption of aroma compounds by polymers is a complex phenomenon. As we have shown in this paper, two complementary methodologies (MHE-PTI and solvent extraction) allow us to establish a complete mass transfer of the aroma compounds during food-packaging contact. Sizer *et al.* (1988) expected that the predominant factor in the change of flavor during storage is the chemical degradation of aroma compounds and the development of off-flavors. Our results demonstrate that the degradation of some aroma compounds (pinenes, geranial, neral) plays a major role. In addition, we established that sorption by polymers of pinenes can be a favorable way to protect them from degradation and to prevent formation of off-odors such as α -terpineol, borneol, and α -fenchol.

ABBREVIATIONS USED

PP, polypropylene; GC, gas chromatography; MHE, multiple headspace extraction; PTI, purge and trap injector; MS, mass spectroscopy, NIST, National Institute of Standards and Technology; MSD, mass selective detector.

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