

Volatile Compounds Extracted from Polypropylene Pellets by Hot Water: Influence of the Level of the Peroxide Agent

P. REBEYROLLE* and P. ETIÉVANT†

Institut National de la Recherche Agronomique, Laboratoire de Recherches sur les Arômes, 21034 Dijon, France

SYNOPSIS

To improve the quality level of plastic packaging materials, we determined the influence of chemical degradation of polypropylene (PP) upon the amount of volatile components extracted by hot water from PP pellets. Two formulations were analyzed and compared: PP CR (degraded) and PP (not degraded). After Likens–Nickerson's extraction of the pellets and concentration of the extract, an HPLC fractionation was made to collect three fractions of different polarities: a pentane (A), a dichloromethane (B), and an ether (C) fraction. Fractions (B) and (C) were olfactively evaluated by GC sniffing to be most interesting. Their analysis by GC/MS coupling allowed the identification of different components: aldehydes, ketones, and phenols in fraction B and alcohols and acids in fraction C. A quantitative analysis gave us the amounts of volatiles that were compared to their olfactive thresholds in water; thus, in fraction (B), nonanal and decanal were concluded to have a potential olfactive contribution to the odor of water in contact with PP. A statistical analysis showed that chemical degradation had little influence upon the amounts of volatiles extracted from PP pellets by hot water.

INTRODUCTION

Recent development with foods directly packaged in plastic films or boxes is the origin of many questions concerning packaging compatibility. These questions, recently summarized by Risch,¹ include concern about the migration of low molecular weight substances (1) from the food through or into the package, (2) from the environment to the food through the package, and (3) from the package to the food.

In the first category, the permeability of plastic packages to oxygen, aroma, and water vapor is preponderant as described by Davis²; the sorption of volatile molecules by plastic materials has also been outlined by Tavss et al.³ for toothpaste, by Hriciga and Stadelman⁴ for coffee, and by Shimoda et al.⁵ for a model flavor solution.

In the second category, Goldenberg and

Matheson⁶ have reported examples of airborne contamination in cakes in which a bad taste was due to volatile components coming from nearby factories. Other cases of off-flavors were due to packaging contamination, e.g., fruit drinks bottled in PVC.

The third category includes specific migrations of additives, monomers, or plasticizers into the food. Figge and Freytag⁷ and Bieber et al.⁸ have studied mainly the migration of phenolic antioxidants from plastics into fatty foods or HB 307 simulant. They quantified the migration by a radio-analytical method and studied the influence of time of contact, surface of contact, temperature, and fat content of the food. Nevertheless, very few investigations concern migration of volatile constituents from the package to the food.

The main topic of this research is therefore to study the migration of such constituents and to determine the influence of plastic composition on their migration.

Polypropylene (PP) was chosen for this study, since it corresponds to 13% of the packaging market in Western Europe today and will likely take a larger part of this market in the coming years, provided that the quality level of this plastic material could

* Current address: Société Française Hoechst, Lillebonne, France.

† To whom correspondence should be addressed.

be improved. It is currently used, for example, to produce coffee machines and containers for margarine, pâté, cream, deserts, and lyophilized foods. Brighton⁹ studied PP in an investigation on butter wrapping materials. Mottar¹⁰ studied the usefulness of coextruded PP as an alternative packaging material for the aseptic packaging of orange juices; Hagman and Jacobson¹¹ used multiple dynamic headspace extractions to quantify volatiles of PP and polyethylene.

The aim of this work was to obtain qualitative and quantitative data about volatiles in PP material. It had three objectives: first, to study the extraction of volatile chemical species of PP by water vapors; second, to select and identify volatile constituents of PP that might alter the quality of food; and third, to investigate the possible influence of a particular additive on this possible alteration—Prémix H, a well-known peroxide agent, used to settle the fluidity of PP.

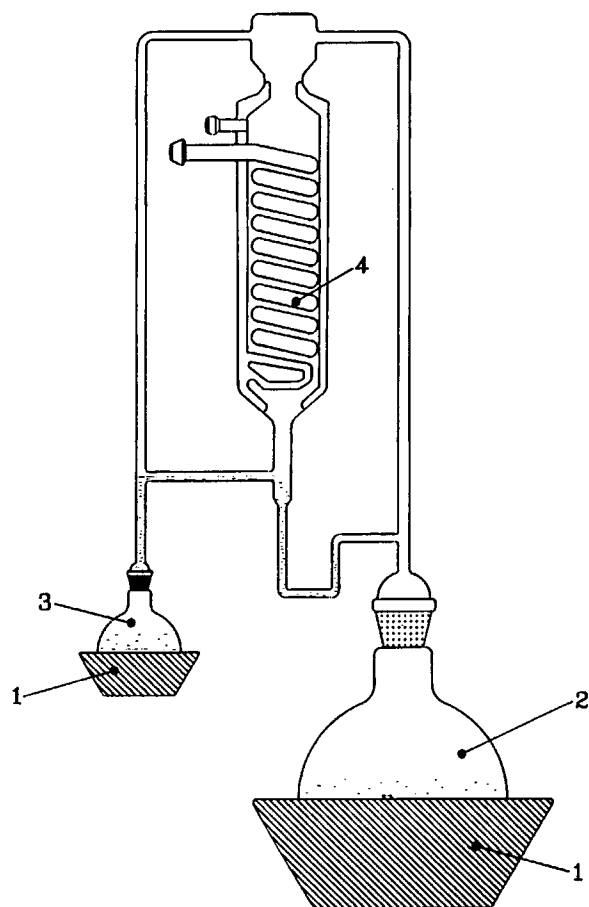


Figure 1 Lickens-Nickerson extractor: (1) electric heaters; (2) flask containing plastic pellets and water; (3) flask containing pentane; (4) condenser cooled with tap water.

MATERIALS AND METHODS

Materials

Two different types of plastic pellets of Hostalen PP (Société Française Hoechst) have been used for analysis. The first one did not contain any peroxide additive (Prémix H) and was called PP; the second one, PP CR, contained 0.22% of Prémix H.

Dichloromethane (99.95% pure) and ether (99.5%) were freshly distilled. Pentane (99.95% pure) was also distilled by the same method, but was previously purified from unsaturated contaminants by several washes with pure sulfuric acid and then with water. Water was purified just before use with a Milli-Q reagent water system using an Organex-Q cartridge (Milli RO4, Millipore).

Extraction of Volatile Components

Volatile components of pellets were extracted using a modified version of the apparatus described by Likens and Nickerson.¹² Pellets, 5 kg, were introduced with 5 L purified water into the 10 L flask, and 500 mL pentane was poured into the 1 L flask (Fig. 1). The beginning of the extraction was determined as the time when both vapors of pentane and water began to condense on the cold part of the body of the extractor. At the end of two similar 5 h extraction periods, the organic phase corresponding to 10 kg of PP pellets was dried with a small amount of sodium sulfate (Rectapur). This total organic extract was concentrated to 2 mL with a Snyder column and was kept at 5°C for further analysis.

HPLC Fractionation

The total organic extract (100 μ L per injection) was separated on a 250 \times 10 mm column packed with silica gel (Intersil Si60, 5 μ m, Interchim) using a Gilson pump model 303. Three fractions were collected corresponding to the percolation of, respectively, 150 mL pentane (fraction A), 150 mL CH_2Cl_2 (fraction B), and 150 mL ether (fraction C). These fractions were, respectively, concentrated as described above down to 4000 μ L (A), 650 μ L (B), and 550 μ L (C) and were stored at 5°C.

Gas-chromatographic (GC) Separation and Odor Evaluation

The constituents of each fraction were separated by GC using a Girdel 300 chromatograph equipped with a DB5 column (25 m \times 0.32 mm i.d., J & W Inc.),

a splitless injector, and a flame ionization detector. Oven temperature was programmed from 40°C to 220°C at 3°C min⁻¹. The amounts of volatiles of each fraction relative to the total extract were estimated from the total GC peak area, obtained with an Enica 21 (DELSI) integrator, and from the volume of the fractions using the following equation:

% of volatiles of fraction *i*

$$= \frac{\sum_{j=1}^n \left[\frac{A_{j,i}}{V_{inj,i}} \times V_i \right]}{\sum_{i=1}^3 \left[\frac{\sum_{j=1}^n A_{j,i}}{V_{inj,i}} \times V_i \right]} \times 100$$

in which $A_{j,i}$ is the area of each peak *j*, except the solvent peak, corresponding to fraction *i*; $V_{inj,i}$ is the volume of fraction *i* injected in the chromatograph; and V_i is the volume of fraction *i*. An outlet splitter also allowed the olfactory detection of volatile compounds eluting from the column as described by Etiévant et al.¹³ Each fraction was injected four times; intensity and description of the odors during a GC run were noted by four different trained persons working in succession for 20 min-long periods. At the end, each person sniffed all the sections of the chromatograms.

Selection of Volatile Constituents and Quantification

Quantification and identification were focused on odors with high intensities that were described as undesirable or unpleasant. Many odors were detected by the GC sniffing of the total extract and of each fraction. Only those detected at the same retention time by three persons out of four were selected for further analysis. The amounts of these selected peaks were determined by comparison of peak areas with a known amount of internal standard (eugenol) added to each fraction before concentration. Statistical significance of differences between concentrations were calculated from analysis of variance.

Identification by Gas Chromatography/Mass Spectrometry (GC/MS)

Each of the three fractions A, B, and C was analyzed by GC/MS. The gas-chromatograph used was a Girdel 31 equipped with a DB5 column (60 m × 0.32 mm i.d., J & W Inc.) and with similar temperature

programming as already described. The transfer line to the source of a Nermag R10-10 mass spectrometer consisted of a platinum capillary tube heated to 300°C. Conditions of ionization were the following: electronic ionization, 70 eV; source temperature, 150°C; and scanning limits, 26–250. Identifications were realized from comparison of sample spectra with published spectra. When pure standard compounds were available, identifications were confirmed by comparison of their spectra acquired on the same instrument and by comparison of their Kovats' indices.

RESULTS AND DISCUSSION

The Likens–Nickerson's extraction was chosen among the numerous techniques used in the field of aroma because it allows the extraction of the product by steam. It is, for example, what happens in a coffee machine in which steam is in direct contact with PP. Preliminary experiments carried out to determine the optimum time for extraction demonstrated that most volatile components were quantitatively extracted in 5 h and that the odor of the extract thus obtained was very similar to that of PP coming out of the polymerization unit before pelletizing.

A preliminary mass spectrometric investigation of the total extract showed that the major constituents of the extract were hydrocarbons (alkyl, alkenyl, and aryl). These were judged as being unlikely responsible for the unpleasant odor noted for all samples of PP pellets.

For this reason, the total extract was separated by HPLC according to the polarities of its constituents on a silica gel column as described by Palmer.¹⁴ The first fraction (A) contained most of the volatiles of the total extract (98.6%), i.e., the hydrocarbons identified by GC/MS. This fraction was judged almost odorless as compared to the total extract. This was confirmed by the few weak odors detected by the GC sniffing. Fraction A was therefore discarded from further analyses. The second fraction, fraction B, was quantitatively minor (1.2%), but exhibited a strong and unpleasant odor. The results of sniffing showed that all odors previously detected in the total extract could also be noted in fraction B. Because of the very large number of the compounds, and because the main interest was in those pellet constituents that might produce taints in food, efforts of identification were focused on compounds producing intense and unpleasant odors as detected by GC sniffing. The odorous compounds in this fraction identified by GC/MS are given in Table I along with

Table I Identification and Odor Description of Selected Constituents of Fraction B

Volatiles Components Selected in Fraction B	Kovats Indices	Odors Detected by Sniffing, Intensities (0-5)		Odors Described for the Pure Compounds ¹⁵
Heptanal ^a	903	Floral, hot plastic, rubber	2	Harsh, fatty, rancid taste in high concentration, sweet almondlike
4-Methyl-2-heptanone	954	Tar, washing powder	3.5	
A methyl ketone	973	Burnt wood, hot plastic, sour	3.5	
Octanal ^a	1004	Unpleasant, sweet, insecticide	3.5	Powerful, and in indiluted state, harsh, fatty, penetrating odor. In extreme dilution, sweet orangelike, slightly fatty
Nonanal ^a	1103	Plastic packaging, pungent, oil	4	Very powerful and diffusive fatty floral waxy odor of moderate tenacity. In proper dilution, fatty notes become more pleasant
Decanal ^a	1203	Lemon, mushroom, hot plastic, burnt, rubber, rancid	3	Penetrating and very powerful sweet, waxy, orange-peel-like odor. In extreme dilution, refreshing, citrus peel-like
Undecanal ^a	1304	Rubber, hot plastic, bitter orange	3	Pleasant waxy floral, refreshing odor with a discrete fruity overtone and moderate tenacity. Citrusy fresh taste
Dodecanal ^a	1409	Lemon, pungent	4	Sweet, waxy, herbaceous, very fresh and clean floral odor with a faint balsamic undertone
2,6- <i>t</i> -Butyl quinone ^a	1471	Pungent, burnt, wet paper	4	
2,6- <i>t</i> -Butyl phenol	1509	Tar, rubber, ink, nut, insecticide, wood	2	
Tetradecanal ^a	1610			
2,6- <i>t</i> -Butyl ethyl phenol	1770			
2,6- <i>t</i> -Butyl propyl phenol	1820			

^a Kovats indices of the natural compounds did not differ from the pure compound by more than 5%. Others could not be checked since references were not available.

their Kovats' indices. Also, the odor descriptors as determined by GC sniffing are compared to those reported in the literature.¹⁵ Compounds selected for their intense unpleasant odors were mainly linear alkanals (C7-C14) and di-substituted alkylphenols, but also methylketones and one quinone. The terms used to describe the odors sniffed by GC differed from those reported in the literature, although some similarities did exist. These differences may be because the descriptors in Arcander's book¹⁵ correspond to odors of aqueous solutions, i.e., ones in a different medium, at different concentrations, and different temperatures than those involved during sniffing the GC effluent. None of these compounds exhibited the characteristic odor of the pellets, thus indicating that the global odor was probably due to the sum of several individual odors.

The amounts of these selected compounds extracted from pellets differing in their Premix H content are given in Table II. The result of the analysis of variance performed on these amounts is also given. The total amount of the compounds extracted from 1 kg pellets by 1 L water does not exceed 88 µg. 2,6-*t*-Butyl quinone (35.9 µg/L) and 2,6-*t*-butyl phenol (21.1 µg/L) represent the major components of the fraction. Their olfactive contribution as that of some other compounds (Table II) could not be assessed since their olfactive thresholds were not available. The comparatively low concentrations of nonanal and decanal may contribute to the unpleasant pellet odor since their respective odor detection thresholds are even lower.¹⁶ For other compounds as heptanal, octanal, and undecanal, their detection thresholds are also low, but higher than their con-

Table II Fraction B: Quantification of Some Volatile Constituents Extracted from PP and PPCR Pellets

Volatile Components Selected in Fraction B	Concentrations of Volatile Components Extracted from 1 kg Pellets by 11 Water ($\mu\text{g} \times \text{L}^{-1}$)		Detection Thresholds in Water ^a ($\mu\text{g} \times \text{L}^{-1}$)	Significance of the Difference ^b
	PP	PP CR		
Heptanal	2.23	2.04	3.0	NS
4-Methyl-2-heptanone	2.39	2.27		NS
Unknown methyl ketone	1.89	2.47		*
Octanal	0.44	0.47	0.7	NS
Nonanal	4.18	4.28	1.0	NS
Decanal	0.95	0.97	0.1	NS
Undecanal	1.28	1.27	5.0	NS
Dodecanal	0.43	2.21	2.0	**
2,6- <i>t</i> -Butyl quinone	35.9	36.1		NS
2,6- <i>t</i> -Butyl phenol	21.1	21.2		NS
Tetradecanal	0.95	1.05		NS
2,6- <i>t</i> -Butyl ethyl phenol	10.08	10.12		NS
2,6- <i>t</i> -Butyl propyl phenol	3.28	3.39		NS
Total	85.1	87.8		

^a Guadagni et al.¹⁶

^b NS = not significant. * $P < .05$, ** $P < .01$.

centrations. Their olfactive contribution is therefore probably less important than that suspected for nonanal and decanal, but cannot be totally ignored.

Fraction C is quantitatively the smallest (0.2%). It nevertheless had an odor of unnegligible intensity. As for fraction B, only compounds with unpleasant

or intense odors were investigated by GC/MS. Results of sniffing and identifications are given in Table III. The selected compounds are alcohols and acids as expected in this more polar fraction; their concentrations and detection thresholds are given in Table IV. As already mentioned for fraction B, de-

Table III Identification and Odor Description of Selected Constituents of Fraction C

Volatile Components Selected in Fraction C	Kovats Indices	Odors Detected by Sniffing, Intensities (0-5)		Odors Described for the Pure Compounds ¹⁵
Decanol ^a	1272	Rubber, tar, soap, camphor menthol	2	Sweet, slightly fatty-oily odor, waxy and floral, mainly rosy, fresh
Dodecanol	1475	Pleasant, sweet, bitter orange, peach, apricot	3	Very mild, oily-fatty, slightly waxy but fresh and remotely "soapy" odor
Tetradecanol	1679	Soap, detergent, washing powder	3	
Tetradecanoic acid ^a	1758	Pungent, sulfur, tobacco	3	
Hexadecanol	1881	Pungent, soap, menthol	2	Faint, sweet, oily odor and bland taste
Hexadecanoic acid ^a	1946	Green, rotten		
Octadecanol	2084			Virtually odorless when pure

^a Kovats indices of the pure compounds did not differ from that of the pure compounds by more than 5%. Others could not be checked since references were not available.

Table IV Fraction C: Quantification of Some Volatile Constituents Extracted from PP and PPCR Pellets

Volatile Components Selected in Fraction C	Amounts of Volatile Components Extracted from 1 kg Pellets Water ($\mu\text{g} \times \text{L}^{-1}$)		Detection Thresholds in Water ($\mu\text{g} \times \text{L}^{-1}$)	Significance of the Difference ^a
	PP	PP CR		
Decanol	3.67	3.68	8.2–6.6 ^b	NS
Dodecanol	4.45	4.55	81.8–40.9 ^b	NS
Tetradecanol	1.41	1.42		NS
Tetradecanoic acid	6.50	7.60	10.0 ^c	**
Hexadecanol	4.87	4.88		NS
Hexadecanoic acid	11.12	11.13		NS
Octadecanol	94.2	95.4		NS
Total	126.22	128.66		

^a NS not significant: ** $P < .01$.

^b Schnabel et al.¹⁷

^c Cherkinsky.¹⁸

scriptors obtained from GC sniffing and those given in the literature were not the same. As previously noted, none of these compounds had the characteristic odor of the pellets, but exhibited pungent, rotten, or soapy notes that might contribute to their unpleasant odor. The total amount of extracted components is about 127 $\mu\text{g}/\text{L}$ for each formulation. Octadecanol (94 $\mu\text{g}/\text{L}$) is by far the major component of fraction C. Unfortunately, its odor threshold was not found in the literature and it was therefore difficult to evaluate its olfactive impact; the same problem occurs for tetradecanol, hexadecanol, octadecanol, and hexadecanoic acid. The thresholds of the three remaining components^{17,18} are higher than their concentrations in the fraction, so they probably do not contribute to the odor of the extract (Table IV).

The amounts of the selected compounds that were extracted by 1 L water from 1 kg of the two batches of pellets (PP and PP CR) are itemized in Tables II and IV. They show, as estimated from the analysis of variance, that adding Premix H to the PP blend, i.e., more or less chemically degrading the polymer, has little influence on the concentration of volatiles that may communicate unpleasant odors. Only three of these, e.g., dodecanol, tetradecanoic acid, and, to a lesser degree of probability, an unknown methyl ketone, are significantly different in concentration between the two plastic batches. Tetradecanoic acid varies slightly (6.5–7.6 ppb), and its odor varies probably even less since odor intensity is a function of the logarithm of concentration. Dodecanol is,

consequently, the only compound among the different compounds that might possibly alter the odor of water, since its concentration is slightly higher than its threshold in pellets containing 0.22% Prémix H. However, one must be aware that the surface of contact between the plastic pellets (1 kg) and water (1 L) is certainly much higher than that met in a typical food system, e.g., a coffee machine.

CONCLUSIONS

This study showed that the extract obtained from PP pellets with steam has a strong odor for both formulations involving or not Prémix H. Three fractions of different polarities can be underscored: fraction A (apolar) is the most important quantitatively but shows few olfactive contributions. Fraction B is the most interesting fraction since it is described by GC sniffing by "plasticlike" descriptors. Among the compounds possibly responsible for its odor, dodecanol is the only one for which the concentration differs between PP and PP CR formulations. Fraction C (polar) has an unnegligible odor that was not described with plastic terms during its GC sniffing and for which no difference could be noted in relation with Prémix H addition.

These experiments did not consider further alterations that are susceptible to occur during the injection molding of pellets and to modify the qualitative and quantitative results reported here. A specific investigation is currently made in order to

take into account this technological step for the same formulations (PP and PP CR) at different injection-molding temperatures.

The authors wish to thank Société Française Hoechst (Tour Roussel-Hoechst, Puteaux) for financial support; Drs. G. Krotkine, S. Couturier, and G. Mattioda (Société Française Hoechst) and Pr. F. Pellerin (Université, Chantenay-Malabry) for helpful discussions, and Mrs. J. Dekimpe (INRA Dijon) for valuable technical assistance.

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Received March 28, 1991

Accepted June 17, 1991