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Representativeness of Extracts of Offset Paper Packaging and Analysis of the Main Odor-Active Compounds

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Packagings often carry odors due to the support and printing inks. The aim of the investigation was to define a representative solvent-free extract of paper-based packaging materials printed by the offset process, for the identification of the odor-causing volatile compounds. Static headspace and solid-phase microextraction were the two applied extraction methods. Representativeness tests showed that the odor of the PDMS fiber extract gave satisfying odor similarities with the original packaging. The sample incubation was performed at 40 °C for 30 min, whereas the extraction time was 3 min at 40 °C. Extracts of both the nonprinted and printed papers of different batches were analyzed by gas chromatography−olfactometry. 4-Phenylcyclohexene was identified as the most potent compound contributing to the latex-like odor of the nonprinted paper. Among the 13 major odorants identified by mass spectrometry, 10 were aldehydes and ketones generated by oxidation of the printing ink resins. The ratio of odorants to interferences was too low for a possible detection of the key odorants by nonseparative techniques such as sensor arrays.

KEYWORDS: Representativeness; solvent-free extraction; SPME; odor analysis; olfactometry; offset packagings; paper; ink

INTRODUCTION

Although food packagings now provide an effective safety assurance against microorganisms and biological and chemical external contamination, it has been well-known for many years that the packaging materials can represent a source of odorous and tainting components (*1*). Off-flavors in foods originating from packagings have been largely reviewed in the literature (*2*−*5*). In >50% of complaints from consumers related to off-flavors in foods, packaging is involved (*6*). Many of those claims are the results of an unpleasant smell released when the food package is opened. Even when packaging exhibits high intensity odors, a tainting of the packaged foodstuffs might not be necessarily reported, although the food would be rejected without consumption. In contrast, some odorants responsible for a weak smell of the packaging material can present a high affinity for some packed foods, for example, chocolate, which can then show a strong taint after transfer of the odorants to the food.

Packaging manufacturers and food packers are both aware that the quality control of packaging materials is essential, particularly when they are intended to come into direct or indirect contact with the packed foodstuff. To meet the odor and taint regulations for packaging (*7*) and characterize the potential problems, both sensory and instrumental tests are carried out on the materials after production and prior to use. The common sensory methods to monitor the quality of packaging products are the odor and taint tests (*8*). The odor test allows the intensity of the odor released from a packaging to be determined. The taint test, also called the Robinson test, evaluates the taint transfer or flavor change of the food to be in direct or indirect contact with the material (*9*). Both types of sensory tests are time-consuming and require a well-trained internal or external panel. For the instrumental analysis separation, identification and quantification of the volatile compounds are performed by GC-FID or GC-MS. The sample preparation method greatly depends on the nature of the volatile compounds causing the off-odors or off-flavors. Analysis of residual solvents, components of high odor thresholds and present in large amounts, is hence easily performed from a static headspace gas sample (*10*). For extraction of low odor threshold compounds present at low levels, the common solvent-free enrichment techniques are dynamic headspace (*11*−*14*), direct thermal desorption (*15*), and, more recently, solid-phase microextraction (SPME) (*16*). Concentration methods involving solvents can be applied, that is, solid−liquid extraction (*17*), steam distillation (*18*, *19*), or simultaneous steam distillation−solvent extraction (*20*, *21*). As for sensory testing, instrumental analyses are time-consuming and need expensive instrumentation.

A new complementary approach for the quality control of products is based on chemical sensor arrays, known as "electronic noses" (*22*). A few investigations have already been conducted on the application of such a new technology on

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packaging materials (*23*−*25*). Moreover, the European project Parfum (IT 20.848) aimed at setting up a sensor system coupled with an automatic headspace sampler, devoted to the detection of residual solvents emitted from packagings. The results reported a satisfying prediction of the human sensory assessments and demonstrated the potential ability to use chemical sensors in the quality control of packaging materials (*26*).

The present work was carried out in the framework of the European project ESCAPE (Electronic Sensor System for the Characterization of Packing Emissions, www.escape-project.org). As the followup of the Parfum project, ESCAPE is intended to develop a rapid and reliable instrumentation coupling a sampling system with sensor arrays for the at-line monitoring of residual solvents and off-odors during the production of packaging materials. The developed instrumentations should be applicable to a wider range of packagings manufactured by two printing processes, that is, the rotogravure and offset techniques. The rotogravure inks contain volatile organic solvents so that drying of the print takes place quickly by volatilization. In this case the occurrence of high levels of residual solvents causes unacceptable odor. Lithographic or offset inks are multicomponent systems comprising a hydrocarbon and/or alkyd resin, a vehicle composed of mineral and/or vegetable oils, and pigments and optional additives (*27*). The petroleum-based chemicals do not evaporate, and filtrate into the support, while the alkyd resins and vegetable oils (when present) dry by oxidation and release odor-responsible byproducts, mainly aldehydes and ketones (*1*, *28*). The reason for an off-odor can also be caused by the offset ink pigments and the possible impurities forming, for example, metal chelates.

The aim of this investigation was to identify the volatile compounds that contribute significantly to the odor of an offset label of industrial concern. The identification of the odorous chemicals represents an important preliminary step in the sampling method and sensor development. Basically the selection and optimization of the sampling method make possible the detection of volatile compounds at low levels because the latter are addressed to the sensors in a selective and enriched way.

The characterization and identification of the odor-active compounds are commonly performed by GC−olfactometry (GC-O) and GC-MS. Such a powerful methodology has been applied to board materials (*11*, *19*) and polyethylene (*29*, *30*). However, to our knowledge, no examination of the contribution of volatiles to the odor of offset packaging printed on paper has been done before. A systematic identification of the volatiles emitted from cardboard offset packagings together with a sensory descriptive analysis of the materials was performed by Letourneur (*31*); however, this interesting investigation did not perform a screening of the odorous components by GC-O, which would enable a determination of the key odorants responsible for the different qualities of packaging materials.

Before GC-O is performed, it is first critical to get an extract having an odor that is representative from the initial product. This crucial study is necessary in order to ensure that extracts contain the compounds contributing significantly to the odor of a product or responsible for the differences between several product odors. In the work done on solvent-free enrichment methods applied to food flavor analysis, rarely is highlighted the importance of testing the representativeness of the extracts. However, representativeness evaluation from solvent extracts has been often emphasized in the literature (*32*−*34*). Direct extract olfactometry, a newly developed method, allows the assessment of the representativeness of solvent-free extracts (*35*); Rega et al. named this technique direct GC−olfactometry (*36*). The method consists of introducing, in a GC injector, solvent-free extracts onto a deactivated capillary tube connected directly to an outer sniffing port. The overall extract odor is then evaluated by a trained assessor in comparison to that of the initial product. This representativeness step is a sensorial verification of the extraction conditions, which does not guarantee that the extract composition is identical to that of the product odor.

In this work, the tested headspace samplings for the extract preparation were the static headspace mode (S-HS) and the solid-phase microextraction (HS-SPME) with different fiber types. Therefore, the purposes of the present investigation were (i) to optimize the extraction conditions of S-HS and HS-SPME, (ii) to select the appropriate extraction method providing the most representative extract from the sensory similarity tests, and (iii) to evaluate the odorous contribution of the volatile compounds released from different batches of the same offset label, and this by means of a separative olfactometry method, the olfactometry global analysis. The latter records the panel's detection frequency of each odorous area eluted at the sniffing port; the results depend on the intensity of the odorants and on the differences of sensitivity between assessors (*37*−*39*).

MATERIALS AND METHODS

Materials. The packaging material, used for chocolate tablets, was a paper label printed by the offset process and provided by CPC (Saint-Dié, France). Different batches of the same label were investigated: March and November of 2002 and January, February, and June of 2003. Each label batch was analyzed by using sensory assessment from the normalized odor and taint tests (*8*), by an internal trained panel from the Nestlé factory (Saint-Menet, France). For the odor test, 1000 cm^2 of the printed packaging material was stored in a closed 1-L glass jar for 1 h at 40 °C. The trained assessors were then asked to evaluate the smell of the packaging material in comparison with a reference (empty jar) and to give a score from 0 (no difference with the reference) to 4 (strong difference with the reference). For the taint test, 1000 cm^2 of the packaging material was placed in a 1-L glass jar together with 25 g of grated chocolate for 48 h at 20 °C. The assessors tested the chocolate with their palates in comparison with the reference chocolate (stored without the packaging material) on the same scale from 0 to 4. The different batches were all classified as accepted, that is, with odor and taint test scores of <2.5 (*6*).

The packaging materials were tightly wrapped by four sealed layers of aluminum foil and stored at 3 °C before use.

Sample Preparation. A sample of 100 cm^2 (5 × 20 cm) was cut from one label and introduced into a 20-mL sample vial. The latter was gastight sealed immediately after introduction of the sample. The vials were stored for 24 h at room temperature before use. The same sample preparation procedure was applied for instrumental and sensory analyses. For the sensory tests, the vials were wrapped with aluminum foil to hide the packaging from the assessors' view.

Chemicals. Dichloromethane and all other volatile compounds were purchased from Sigma-Aldrich (L'Isle d'Abeau Chesnes, France) except 4-phenylcyclohexene (Chemsampco, Trenton, NJ). Non-1-en-3-one and 4,5-epoxy-dec-2-enal were synthesized and kindly provided by Nestlé.

Direct Extract Olfactometry (DEO). The DEO method was used to perform the representativeness tests on the odor of the solvent-free extracts. This recent technique consists of connecting a deactivated capillary column (i.d. = 0.32 mm, l = 60 cm; Supelco, Bellefonte, PA) between the injector and sniffing port of a GC (*35*).

The parameters of the DEO device were as follows: injection system, splitless; injector temperature, 240 °C; oven temperature, 240 °C; carrier gas, hydrogen; flow rate, 100 mL/min; transfer line between GC oven and sniffing port, 240 °C. These parameters limited the separation of the volatile compounds in the deactivated capillary column by chromatographic effect. The panelists evaluated hence simultaneously the global odor of all the injected compounds.

Table 1. Fixed Parameters of the Sample Incubation Together with the Tested and Adjusted Extraction Parameters (Headspace Volume and Exposure Time of the SPME Fiber) To Get the Same Intensity between the Extract and Reference Odor

	fixed parameters		headspace vol or fiber exposure time	
method	incubation time (h)	incubation temp (°C)	tested	adjusted
S-HS	1	40	3 mL	2 mL
		60	3 mL	1 mL
PDMS	0.5	40	1 min	3 min
		60	1 min	1 min
PDMS/CAR	0.5	40	3 min	3 min
		60	1 min	1 min
PDMS/DVB	0.5	40	3 min	1 min
		60	1 min	1 min

Two types of vials containing the same packaging sample were prepared, one used as reference and the other for the solvent-free extraction. Prior to each extract injection the assessor was instructed to open the vial containing the reference, smell it, and memorize its odor. The assessor placed then at the sniffing port perceived instantly the injected extract odor obtained from the second vial. The similarity between the reference and extract odors was determined on a 10-cm unstructured scale, anchored with "identical to the reference" on the left and "very different from the reference" on the right. The distances were converted into scores from 0 to 10.

Definition of the Solvent-Free Extraction Conditions. *S-HS Extracts.* The vials were incubated for 60 min without agitation at 40 or 60 °C. The tested volumes of the vapor phase were 1, 2, and 3 mL, sampled manually with a gastight syringe of 1 or 5 mL.

HS-SPME Extracts. The SPME holder and fibers were purchased from Supelco (Bellefonte, PA). The following fibers were used: poly(dimethylsiloxane) (PDMS) 100 μm, Carboxen/PDMS (CAR/PDMS) 75 μm, and PDMS/divinylbenzene (PDMS/DVB) 65 μm. All of the fibers were conditioned before use as recommended by the manufacturer. The vial incubation was performed for 30 min at 40 or 60 °C, without agitation. The SPME device was manually inserted into the sealed vial, and the fiber was exposed to the packaging headspace for 1 or 3 min at the incubation temperature. The fiber was then inserted into the GC injector for thermal desorption at 240 °C for 10 min (injector split after 1 min; split ratio, 50:1). No conditioning of the fibers was necessary after 10 min of desorption.

The different sampling parameters for S-HS and SPME extracts are summarized in **Table 1**.

Sensory Representativeness Tests of the Extracts. *Panel.* Twelve external panelists were first recruited for selection. All had already performed sensory tests, that is, olfactometry and/or descriptive analysis. The selection and training sessions were held in a special air-conditioned sensory room with individual booths.

Panel Selection. Two tests were used for the selection of the panelists. The Bourdon test, aimed at evaluating concentration and reaction speed, consists of lines of dot groups (*40*). The panelists were asked to cross only the groups of four dots. The time for each line was 8 s. The score mean, that is, the number of crossed groups of four dots per line, is generally between 5 and 6. Lower than 5, the score counts as a fail. The second selection test was the European Olfactive Test for the evaluation of the odor sensitivity and recognition (*41*). This test is constituted of 16 sets of four vials. Among the four vials, one only contains the odor. The panelists had to locate the odorant vial and then assign a descriptor to the odor on a list of four different descriptors. The eliminating score is 11 of 16.

Eleven assessors, 10 women and 1 man, were hence selected for the training sessions and representativeness tests.

Panel Training. The panelists were familiarized with packaging odors from odorous packaging materials, through two training sessions, to be able to describe such nonfood odors. A second training type consisted in odor comparisons within pairs of vials containing different or identical packaging materials; one of the two vials was named "reference". The assessors were asked to evaluate the difference/similarity between the two samples using a 10-cm unstructured dissimilarity scale anchored at the left end with "odor close to the reference" and at the right end with "odor far from the reference".

Table 2. Incubation and Extraction Conditions of the Extracts Used for the Training of the Representativeness Test, Together with the Similarity Score (10-cm Scale)

extraction method	incubation time (h)	temp (°C)	headspace vol or fiber exposure time	similarity score (/10)[a]	SD[b]
S-HS	1	40	2 mL	6.3 a	2.8
PDMS	0.5	60	1 min	3.4 b	2.6
PDMS/CAR	0.5	60	1 min	3.7 b	3.4
PDMS/DVB	0.5	60	1 min	6.6 a	2.8

[a] Score mean obtained from the 11 panelists and the 2 repetitions. Scores with the same letter were not significantly different at a level of 5%. [b] Standard deviation.

Table 3. Incubation and Extraction Conditions of the Extracts Used for the Final Representativeness Test, Together with the Similarity Score (10-cm Scale)

method	incubation time (h)	temp (°C)	headspace vol or fiber exposure time	similarity score (/10)[a]	SD[b]
S-HS	1	40	2 mL	6.2 a	2.7
		60	1 mL	4.7 b	2.8
PDMS	0.5	40	3 min	3.5 bc	3.1
		60	1 min	4.4 b	3.1
PDMS/CAR	0.5	40	3 min	2.6 c	2.4
		60	1 min	4.4 b	2.9

[a] Score mean obtained from the 11 panelists and the 3 repetitions. Scores with the same letter were not significantly different at a level of 5%. [b] Standard deviation.

Representativeness Tests. The packaging material used for the representativeness test was the labels manufactured in March 2002. The 11 subjects evaluated the odor quality of each extract in comparison with the odor of the initial packaging product, named the reference.

First, a training of the representativeness tests aimed at familiarizing the panelists with the DEO device, the use of the 10-cm scale, and odor comparison. This training was performed from four different extracts, each in duplicate (**Table 2**). The eight extracts were presented in a random but identical sequence to each panelist for evaluation.

For the final representativeness tests, a dummy sample was first presented to prepare the panelists to the perceived odors. The dummy sample was obtained from the PDMS/DVB fiber, and its result was not taken into account. Six extracts were then evaluated by the assessors for each repetition (**Table 3**). The six extracts were presented according to a Williams Latin-square design for each repetition, to avoid presentation order influence and first-order carry-over effects (*42*). Each extract was presented in triplicate.

Simultaneous Steam Distillation−Solvent Extraction (SDE). The solvent extraction of the volatile components of the labels was performed in a Likens−Nickerson apparatus as described by Rebeyrolle and Etiévant (*21*).

A few labels were smashed to flakes with an office document shredder. A quantity of 30 g of flakes was mixed with 500 mL of purified water and 180 g of sodium chloride (36%) in a 1-L round-bottom flask. A 250-mL round-bottom flask containing 100 mL of purified dichloromethane was placed at the solvent port of the apparatus. The beginning of the extraction was determined as the time when both water and dichloromethane vapors began to condense. The distillation/extraction duration was 1 h. The organic extract was dried over anhydrous sodium sulfate and concentrated to 0.5 mL in a Kuderna-Danish concentrator. The extract was stored at − 20 °C in glass vials before analysis.

Gas Chromatography−Olfactometry (GC-O). GC-O analyses were performed on SPME and dichloromethane extracts of the offset paper labels and their substrate material, that is, the nonprinted paper.

Extracts were injected into an Agilent gas chromatograph (model 6890, Agilent, Avondale, PA) equipped with a split/splitless injector, a flame ionization detector (FID), and a sniffing port supplied with humidified air (50 mL/min). The volatile compound separation was alternatively performed on two capillary columns: DB-Waxetr (30 m × 0.32 mm, 1 μm) and DB-5 (30 m × 0.32 mm, 1 μm) (J&W Scientific Inc., Folsom, CA). The chromatographic conditions were as follows: injector temperature, 240 °C; split/splitless mode; purge time, 1 min; split ratio, 50:1; FID temperature, 250 °C; carrier gas, hydrogen; velocity, 36 cm/s (35 °C); constant pressure, 43 kPa. From 35 °C the DB-Waxetr column temperature was increased at 10 °C/min to 110 °C, then at 5 °C/min to 180 °C, and finally at 10 °C/min to 220 °C for 15 min. For the DB-5 column the oven temperature was programmed from 40 to 240 °C at a rate of 5 °C/min with a final hold time of 10 min. The GC effluent was split 1:1 at the end of the column between the FID and the sniffing port. Connections between the column and the sniffing port and between the column and the FID were realized with a deactivated capillary column (60 cm × 0.32 mm). The transfer line between the GC oven and sniffing port was kept at 240 °C. A hydrocarbon mixture from C_7 to C_{26} was injected into both capillary columns for the calculation of the retention index of the odorous areas.

The olfactometry global analyses were performed by 10 judges of the same trained panel as for the representativeness tests. The duration of the sniffing was 30 min. The judges were asked to assign odor descriptions to each detected odorous area. The olfactometric data, that is, the detection frequency, correspond to the number of assessors who detect the same signal (*37*). The detection threshold of an odor at the sniffing port was set at 3 for a panel of 10 assessors.

Gas Chromatography−Mass Spectrometry (GC-MS). MS analyses were performed on a 6890 Agilent gas chromatograph coupled with a mass selective detector (MSD 5973, Agilent Technologies). The inlet was operated in the split/splitless mode. The valve delays were 1 and 0.5 min for SPME and solvent extracts, respectively. The carrier gas was helium kept at constant pressure (velocity = 38 cm/s). The two capillary columns and oven conditions were the same as for the GC-O experiments. The MSD conditions were as follows: ionization mode, electron impact; ionization energy, 70 eV; source temperature, 230 °C; scan range, 29−380 amu; scan rate, 2.1 scan/s. The temperature of the transfer line between GC and MS was set at 240 °C. The single ion monitoring (SIM) was applied for the identification of oct-1-en-3-one, (*E*)-non-2-enal, 4,5-epoxydec-2-enal, 4-hydroxy-2,5-dimethyl-2*H*-furan-3-one (Furaneol), and 3-hydroxy-4,5-dimethyl-5*H*-furan-2-one (sotolon).

The odor-active compounds were identified by their retention index and odor descriptor and by comparison of their mass spectra with those of the Wiley database.

Statistical Analysis. SAS (release 8.1; SAS Institute Inc., Cary, NJ) was used to perform the statistical analyses, that is, two-way analysis of variance (according to the model: similarity = product + subject + product × subject) and multiple comparison of means by the Student−Newman−Keuls test.

RESULTS AND DISCUSSION

Generally speaking, a SPME does not guarantee a representative sampling as recoveries vary from one compound to another due to their different partition coefficients in the various phases (sample, air, fiber coating). For instance, Rega et al. (*43*) reported that the static headspace method provided more representative extracts of the orange juice odor than SPME. As a given odor may result from different compositions of volatile compounds, an ideal representativeness study should involve both a quantitative and a sensorial comparison of the extract with the real odor. In the present case, the quantitative test was below the capabilities of analytical instruments, due to the extremely low concentration of some important odorants that are introduced below. Therefore, only sensorial tests were performed to adjust the extraction conditions that ensure the best possible representativeness.

Determination of Extraction Conditions. The determination of the extraction conditions represented a preliminary and essential work for the representativeness tests. Basically, before the latter were begun, the extraction conditions had to be fixed in order to get for both the extract and the reference odors of similar intensities. Different intensities for the two odors would have induced biases into the panelists' answers for odor comparisons, and panelists had to focus on the odor quality while performing the representativeness tests.

The extraction parameters to be defined were the volume of headspace to be sampled for the S-HS extracts and the exposure time of the SPME fiber for the HS-SPME extracts. The fixed parameters were the time and temperature of incubation of the samples (**Table 1**). The odor intensity evaluation was performed with the DEO device.The experiments were performed with nine in-house assessors experienced in sniffing procedures and odor description. The panelists were instructed to focus on the odor intensities and hence to mention whether the intensity of the extract odor, in comparison with that of the reference, was lower, similar, or stronger. According to their answers the extraction conditions were adjusted if necessary.

Agreements on odor intensity descriptions between the assessors were difficult. The adjusted extraction conditions correspond to the parameters providing extracts with odor intensities most similar to that of the extracts (**Table 1**).

Representativeness Tests of the Extracts. *Training Session.* The results of the training session for the similarity test are presented in **Table 2**. The lower the score, the higher is the similarity between the extract and reference odors. The most representative extracts were obtained from the PDMS and PDMS/CAR fibers (respectively, 3.4 and 3.7). The extracts obtained by S-HS and with the PDMS/DVB fiber gave the worst representativeness results (respectively, 6.3 and 6.6). The PDMS/DVB fiber was removed from the final tests because this fiber did not provide a representative extract of the original product. The S-HS extraction method was, however, maintained in the final test because it represented a reference method based on the headspace analysis of the packaging materials.

Final Tests. The final similarity scores are displayed in **Table 3** and confirmed those obtained during the training session (**Table 2**). The product effect was significant ($F = 6.7$, $p < 0.0001$) with only a slight subject effect ($F = 1.9$, $p < 0.0494$) and no interaction ($F = 1.1$, $p < 0.2456$). The S-HS extract at 40 °C presented the lowest odor representativeness in comparison with the odor reference, with a similarity score of 6.2. At 60 °C, the increase in the representativeness of the odor headspace (score of 4.7) is likely to be due to a higher and more representative release of the volatile compounds responsible for the packaging odor. In a study devoted to the representativeness of orange juice extracts, Rega et al. (*43*) revealed that the most representative extract was obtained from the static headspace method and not from SPME. The choice of the extraction method depends greatly on the matrix and volatile compound nature.

The scores obtained for the extracts S-HS, PDMS/CAR, and PDMS at 60 °C and for PDMS at 40 °C were evaluated to be not significantly different ($p < 0.05$). In addition, the odor of the PDMS extract at 40 °C was assessed as being not significantly different ($p < 0.05$) from that of the PDMS/CAR extract at 40 °C. The PDMS and PDMS/CAR fibers gave hence the best results for the packaging odor representativeness.

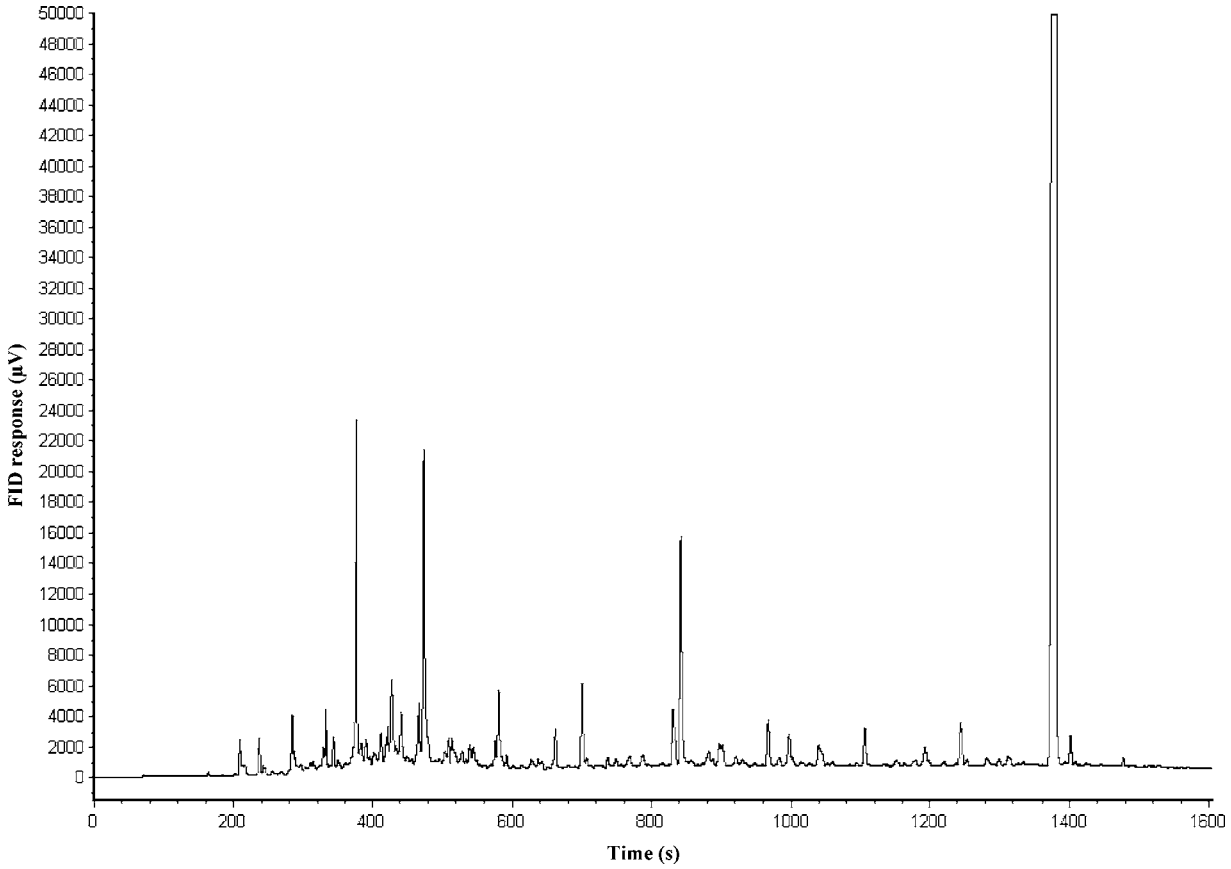

Figure 1. GC profile of HS-SPME extract (PDMS fiber) obtained with the February 2003 label.

The selected extraction method was the HS-SPME technique using a sample incubation temperature of 40 °C and the PDMS fiber. Although the PDMS/CAR fiber appears to be the method providing the best similarity scores, it was not chosen because this fiber is known to present a decreasing adsorption capacity with increasing extraction numbers. Those modifications seem to be attributable to a loss of accessible surface of the Carboxen pores (*44*). The choice of the PDMS/CAR fiber would require the regular use of a standard mixture to check the adsorption capacity of the fiber. The PDMS fiber allows a high extraction number (up to 100) without variation in the absorption capacity of the nonporous polymeric sorptive layer (*45*).

As the tests of representativeness were realized from one label batch (March 2002 production), the extraction conditions providing representative extracts were checked on another batch. A second set of representativeness tests was performed for the March 2002 and January 2003 labels and for the nonprinted paper (January 2003 batch). The samples were also incubated at 40 °C for 30 min, and the exposure time of the PDMS fiber was 3 min at 40 °C. The mean scores for the printed labels (March 2002 and January 2003) and the nonprinted paper were 4.2, 2.9, and 3.8, respectively. The means were not significantly different ($p < 0.05$) and fell within the previous data obtained only from the March 2002 label. Conclusively, the resulting extraction conditions provided satisfying representative extracts from different label productions and could be applied for both the printed labels and the nonprinted support.

Identification of Odor-Active Compounds. The odor-active compounds were first extracted for MS analysis by using the PDMS fiber (**Figure 1**). The identification results were very limited considering the large interference induced by the ions with *m*/*z* values of 43, 57, 71, and 85, which correspond to the C−C bond breaking of hydrocarbons. The sources of hydrocarbons are (i) the offset ink and (ii) the wood and fiber raw materials used in paper and board manufacturing (*46*).

The SDE method was hence subsequently applied because it avoids a direct extraction with an organic solvent (trapping all of the hydrocarbon products) and leads to a better release and recovery of the water-soluble odorant volatiles, such as the unsaturated aldehydes and ketones. Consequently, most of the odorants were identified from the SDE extracts, by GC-MS. The retention index and odor descriptor of the molecules of interest for identification were checked by GC-O to be common to the PDMS and the SDE extracts.

Analysis of the Paper Support. The analysis performed by olfactometry global analysis on the nonprinted paper used for the November 2002 and January 2003 productions revealed only one strong odorous area with a detection frequency of 10 (for 10 panelists), due to 4-phenylcyclohexene with a green/latex characteristic odor (**Table 4**). Hence, one key odorant was responsible for the paper odor.

4-Phenylcyclohexene is a byproduct of the polymerization process between styrene and butadiene; the resulting copolymer is a synthetic resin binder commonly used for the surface coatings of papers and boards. This hydrocarbon represents a typical off-odor compound of latex coated papers (*1*, *4*, *28*).

Three odorous peaks were significantly perceived from the nonprinted paper used for the February 2003 label production. The responsible odorants were (*E*,*E*)-hepta-2,4-dienal, 4-phenylcyclohexene, and 4,5-epoxydec-2-enal. The two unsaturated aldehydes could result from oxidation of unsaturated fatty acids and other constituents of wood resins (*4*). However, the additional presence of (*E*,*E*)-hepta-2,4-dienal and 4,5-epoxydec-2-enal in the February batch of paper did not change its characteristic latex-like odor. The three paper batches came from the same manufacturer, and changes in the process, storage, and

Table 4. Odor Detection Frequency Results on the Paper Supports from the November 2002, January 2003, and February 2003 Labels and Identification of the Odor-Active Compounds

peak	RI[a]	compound	identification method	odor description[b]	DF[c] Nov 2002	DF[c] Jan 2003	DF[c] Feb 2003
1	1540	(*E*,*E*)-hepta-2,4-dienal	SDE,[d] RI,[e] odor[f]	oily, green, paper			5
2	1802	4-phenylcyclohexene	PDMS,[g] SDE,[d] RI,[e] odor[f]	green, latex	10	10	9
3	2045	4,5-epoxydec-2-enal	SDE,[d,h] RI,[e] odor[f]	metallic			9

[a] Retention index of the odorous area on a DB-Waxetr column. [b] Odor description at the sniffing port. [c] Detection frequency of 10 panelists. [d] MS analysis on the SDE paper extract. [e] Retention index of the standard on a DB-Waxetr column. [f] Odor of the standard. [g] MS analysis on the PDMS paper extract. [h] Comparison with the mass spectrum of the pure standard.

Table 5. Odor Detection Frequency Results on the Four Labels, March 2002, November 2002, January 2003, and February 2003, and Identification of the Odor-Active Compounds

peak	RI[a]	compound	identification method	odor description[b]	DF[c] March 2002	DF[c] Nov 2002	DF[c] Jan 2003	DF[c] Feb 2003
1	1086	hexanal	PDMS,[d] SDE,[e] RI,[f] odor[g]	green	9	4		
2	1322	oct-1-en-3-one	RI,[h] odor[g]	mushroom	7	5	5	9
3	1383	unknown		metallic, green	4			
4	1464	(*E*)-oct-2-enal	SDE,[e] RI,[f] odor[g]	floral, soap, green	8	4	4	6
5	1492	unknown		green, petroleum	4			
6	1538	(*E*,*E*)-hepta-2,4-dienal	SDE,[e] RI,[f] odor[g]	oily, green, paper	3			6
7	1568	(*E*)-non-2-enal	SDE-SIM,[i] RI,[h] odor[g]	vegetal, paper	9	8		5
8	1599	unknown		fruity, floral				4
9	1623	octa-3,5-dien-2-one	SDE[e]	green, floral	4	4		4
10	1696	unknown		petroleum	6	3	5	5
11	1716	unknown		paper, earthy, oily	5			
12	1740	(*E*,*E*)-nona-2,4-dienal	SDE,[e] RI,[h] odor[g]	oily, green	7	7		6
13	1800	4-phenylcyclohexene	PDMS,[d] RI,[h] odor[g]	green, latex	9	8	9	10
14	1858	(*E*,*E*)-deca-2,4-dienal	SDE,[e] RI,[h] odor[g]	oily	3	3	4	5
15	1995	unknown		fruity, floral				4
16	2042	4,5-epoxydec-2-enal	SDE-paper,[j,k] RI,[h] odor[g]	metallic	4			8
17	2066	2,5-dimethyl-4-hydroxy-2*H*-furan-3-one	RI,[h] odor[g]	caramel		3		6
18	2106	unknown		vegetal, chemical	4			
19	2248	3-hydroxy-4,5-dimethyl-5*H*-furan-2-one	RI,[h] odor[g]	walnut, spicy		6		10

[a] Retention index of the odorous area on a DB-Waxetr column. [b] Odor description at the sniffing port. [c] Detection frequency of 10 panelists. [d] MS analysis on the PDMS label extract. [e] MS analysis on the SDE label extract. [f] Retention index of the standard on a DB-Waxter column. [g] Odor of the standard. [h] Retention index check with the standard on DB-Waxetr and DB-5 columns. [i] MS analysis on the SDE label extract in SIM mode. [j] MS analysis on the SDE extract on the nonprinted paper. [k] Comparison with the mass spectrum of the pure standard.

transport conditions may explain the reported qualitative differences. An additional source of unsaturated aldehydes would be the presence of recycled materials containing residues from printing inks (*46*).

A study on the mechanisms of paper odor release reported that paper material appeared to be unable to store volatile aldehydes and that the latter were hence formed during the analytical procedure (*47*). These findings rely on trials carried out at varying conditions: incubation time (≤24 h), incubation temperature (≤80 °C), and paper amount in the vessel (≤40 g, higher paper capacity of the 600-mL vessel). In the present work, such significant formation seems not to be realistic because the samples in vials were kept for 24 h at room temperature (∼25 °C) before their incubation at 40 °C for 30 min. Our incubation time and temperature appear to be not drastic enough to induce the formation of a detectable amount of volatiles.

Comparison of the Four Packaging Batches. The results of the odor detection frequency method for the four packaging labels are summarized in **Table 5**. Nineteen odorous areas were perceived by at least 3 of the 10 panelists.

Oct-1-en-3-one (peak 2), (*E*)-oct-2-enal (peak 4), and 4-phenylcyclohexene (peak 13), with detection frequencies from 3 to 10, were perceived within the four label batches. Two additional compounds, unknown **10** and (*E*,*E*)-deca-2,4-dienal (peak 14), were detected within each batch but presented lower intensities (detection frequency from 3 to 6). These five compounds contribute constantly to the overall odor of the studied offset packagings and were the only potent compounds found in the January 2003 batch. The compounds appearing exclusively in the three other batches, March 2002, November 2002, and February 2003, were (*E*)-non-2-enal (peak 7), octa-3,5-dien-2-one (peak 9), and (*E*,*E*)-nona-2,4-dienal (peak 12).

The unknown peaks 3, 5, 11, and 18 were detected in only the March 2002 label and may be oxidation byproducts generated during storage. The storage of this batch lasted one year before GC-O analysis. Considering those aspects the March 2002 batch was considered to be a "nonfresh" sample and was not fully studied during the odorant identification step.

The unidentified odorous areas 8 and 15 occurred once among the four batches, in the February 2003 label, at a relatively low detection frequency (DF = 4).

Most of the identified compounds, hexanal, oct-1-en-3-one, (*E*)-oct-2-enal, (*E*,*E*)-hepta-2,4-dienal, (*E*)-non-2-enal, octa-3,5-dien-2-one, (*E*,*E*)-nona-2,4-dienal, (*E*,*E*)-deca-2,4-dienal, and 4,5-epoxydec-2-enal, are formed during offset ink drying by unsaturated fatty acid oxidation at the material surface. Hence, volatiles from lipid oxidation mainly contribute to the offset packaging odor. Some of those compounds, that is, hexanal,

Table 6. Odor Detection Frequency Results Obtained from the June 2003 Label from DB-Waxetr and DB-5 Capillary Columns

				DB-Waxetr		DB-5	
peak	compound	identification method	odor description[a]	RI[b]	DF[c]	RI[b]	DF[c]
1	oct-1-en-3-one	RI,[d] odor[e]	mushroom	1321	7	973	9
2	non-1-en-3-one	RI,[f] odor[e]	mushroom			1076	4
3	(*E*)-non-2-enal	SDE-SIM,[g] RI,[d] odor[e]	vegetal, paper	1573	3	1156	6
4	unknown		grassy, moldy	1488	4		
5	(*E*,*E*)-nona-2,4-dienal	SDE,[h] RI,[d] odor[e]	oily, green	1736	7	1214	5
6	4-phenylcyclohexene	PDMS,[i] SDE,[h] RI,[d] odor[e]	green, latex	1800	8	1345	8
7	(*E*,*E*)-deca-2,4-dienal	SDE,[h] RI,[d] odor[e]	oily	1848	2	1316	4
8	4,5-epoxy-dec-2-enal	RI,[d,j] odor[e]	metallic	2045	2	1376	9
9	unknown		pencil-like, ink-like			1433	6

[a] Odor description at the sniffing port. [b] Retention index of the odorous area on a DB-Waxetr or DB-5 column. [c] Detection frequency of nine panelists. [d] Retention index check with the standard on DB-Waxetr and DB-5. [e] Odor of the standard. [f] Retention index of the standard on the DB-5 column. [g] MS analysis on the SDE label extract in SIM mode. [h] MS analysis on the SDE label extract. [i] MS analysis on the PDMS label extract. [j] Comparison with the mass spectrum of the pure standard.

(*E*)-oct-2-enal, (*E*,*E*)-hepta-2,4-dienal, (*E*)-non-2-enal, (*E*,*E*)-nona-2,4-dienal, and (*E*,*E*)-deca-2,4-dienal, were previously found in offset-printed materials (*31*) and also in nonprinted paper and board products (*11*, *19*, *46*). However, in the present investigation the nonprinted paper material analyzed contained few oxidative byproducts; only hepta-2,4-dienal and 4,5-epoxydec-2-enal were detected in one paper batch.

Furaneol and sotolon were not perceived during GC−sniffing experiments on the nonprinted paper. It is then assumed that they come from one constituent of the offset ink and this for the November 2002 and February 2003 productions of the studied labels.

The GC-O sessions performed with the February 2003 label revealed 14 potent odorous areas, which is important in comparison with the other labels (**Table 5**). Difference sensory tests would have been a solution to determine whether different olfactometry profiles can induce different overall odor quality. We could have concluded regarding the impact of the qualitative and quantitative differences observed by GC-O on the overall odor. This type of test was not applicable in our case because the label batches underwent different storage times and oxidation reactions still occurred during storage. A GC-O run done on stored February 2003 labels (storage at 3 °C under multiple aluminum foil layers) revealed the presence of an herbaceous odor at RI = 1086, which was not present earlier. This herbaceous odor is characteristic of hexanal, byproduct of unsaturated fatty acid oxidation. A freezing of the labels might have been necessary to reduce the oxidation rate within the inks and/or paper followed by difference sensory tests such as triangle tests.

Olfactometric Analysis on DB-Waxetr and DB-5 Capillary Columns. A complete GC-O analysis of the offset label was achieved by the use of polar and nonpolar stationary phases. The label from the June 2003 production was hence investigated by GC-O from the DB-Waxetr and DB-5 phases to detect the presence of possible other odorous peaks. Odor-active compounds from the June 2003 label are presented in **Table 6**. Nine odorous areas were revealed from both GC phases by nine panelists with frequencies of detection >3.

Non-1-en-3-one was suspected to be the compound responsible for the odorous peak 2 because its retention index and its odor description matched our finding from the DB-5 phase. No further confirmation concerning the presence of non-1-en-3-one could be made from the DB-Waxetr column as this odorant was not perceived from this polar phase. The extremely low threshold of this unsaturated ketone (8 pg/kg) and its very low concentration in food matrices explain why spectral identification and evidence were rarely given (*48*). Another indication of its presence in offset packagings is the likely generation of this odorant from unsaturated fatty acid oxidation (*48*). This odorant was also reported to be produced during thermal oxidation of polyethylene and one of the odor-active compounds responsible for the off-odor of oxidized polyethylene (*29*).

A second odorous area, which was not detected from the DB-Waxetr column, concerned peak 9 characterized by a pencil-like and ink-like odor (**Table 6**). This odor was recognized by certain panelists as being one of the descriptive notes of the product. It has been then checked that the same odorous area was reported in the other offset labels. The responsible odor-active compound was not identified because it was present at trace level.

In this work, the best sensorial representativeness of offset label odors was obtained using a SPME extract with PDMS fiber. Generalization of the findings to SPME extractions, or to other matrices, would be improper. Theoretically, an a posteriori validation of the extract representativeness could be achieved by recombining the different impact odorants determined by the GC-O analysis and comparing both odors of the packaging and recombination. As no quantification was performed in this work and certain odorants remained unidentified, such a recombination was not undertaken.

Application of GC-O to the offset label extract revealed an overall number of 18 odor-active areas in the gas chromatograms of all the studied labels except the March 2002 product. Attempts to identify five odorous areas failed; their retention indices were 1488, 1599, 1696, and 1995 on the DB-Waxetr phase and 1433 on the DB-5 phase. The failure was mainly due to their presence at low levels and the interference caused by hydrocarbons. The identification work revealed that oct-1-en-3-one, (*E*)-oct-2-enal, (*E*)-non-2-enal, an unknown compound at RI = 1696 (DB-Waxetr phase), (*E*,*E*)-nona-2,4-dienal, 4-phenylcyclohexene, (*E*,*E*)-deca-2,4-dienal, and an unknown compound at RI = 1433 (DB-5 phase) represented the most potent and common odorants in the offset labels.

Two important conclusions of this identification work were the presence of (i) the offset packaging key odorants at trace level and (ii) interferences, that is, the hydrocarbon fractions of the printing inks. Therefore, the ratio of odorants to interferences becomes too low for a possible detection of the key odorants by nonseparative techniques such as sensor arrays. The solution for such detection would be the setup of a highly selective enrichment method prior to detection.

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