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Set-off of non volatile compounds from printing inks in food packaging materials and the role of lacquers to avoid migration

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ABSTRACT

Inks are commonly used in food packaging materials and therefore, migration of ink components to food must be studied. Migration from different multilayer materials containing inks to 2 food simulants (ethanol 95% and to Tenax®) was performed, the effect of ink transference and how it was affected by the presence of lacquers in the material was studied. A total of 17 migrants coming from inks due to a set-off phenomena were found in migration from multilayer material [ink/PET/aluminum/polyethylene]. The number of migrants decreased dramatically when a lacquer was added [lacquer/ink/PET/aluminum/polyethylene] and especially when ink was placed under a PET layer [lacquer/PET/ink/aluminum/polyethylene]. Some new migrants appear by the reaction between ink and lacquer. In material [ink/paper/OPP/Al/PE], when a lacquer was added some migrants decreased but other migrants present both in lacquer and ink increased.

1. Introduction

Migration from food packaging materials to food has been widely studied due to the risk that the presence of toxic compounds in food has in consumer health. Food packaging materials are often multilayer materials and are manufactured by the combination of different polymers, commonly joined by adhesives layers. In addition, printing inks, which provide information about the packaged food, are present in most packaging. When multilayer materials are used in food packaging, migration can take place, not only from the internal side of the packaging (food contact surface) but also from internal layers due to diffusion and partition processes [1–4]. In the case of inks, which are applied on the external side of the packaging, an ink transference from the external side to the internal side (side in contact with food) can take place during materials production and storage in rolls, increasing the possibility of ink components migration to food. The transference of inks components from the external printed surface of food packaging to the food-contact surface is called set-off.

Inks, defined as a colored fluid or paste used for writing, drawing or printing, are mainly composed by a pigment or dye, suspended or dissolved, in a solvent. Many works related to the quantification of food and beverages coloring dyes by HPLC have been performed [5–9].

The use of printing inks for food packaging is regulated by the European Printing Ink Association (EuPIA) [10]. Different groups of raw materials can be used in the manufacture of food packaging inks such as additives, colorants, (pigments, dyes), pigment additives, polymeric resins, solvents or photo-initiators [11]. Even when only allowed materials are used, migration studies are necessary, since non intentionally added substances (NIAS) can migrate to food. NIAS can come from impurities of raw materials, degradation processes, chemical reactions between material components or contamination processes [12] and they can be a risk for consumers health.

Set-off phenomena are not visible to human eyes and several works have been performed in order to detect it. Bentayeb et al. detected 7 different compounds coming from inks set-off by ambient ionization-accurate mass spectrometry (AMI-AMS) and confirmed them by GC-MS [13]. Time-of-flight mass spectrometry (DART/TOF-MS) has also been used to detect the non-visible set-off of photoinitiators on the food contact surface of three different packages [14]. An optical approach to excite and observe

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luminescence from invisible set-off was used by Bradley et al [15].

In this work, the set-off phenomena and the further migration to food have been evaluated. Migration experiments were performed and non volatile compounds were analyzed in food simulants. When non volatile unknowns need to be identified, liquid chromatography coupled to high resolution mass spectrometry techniques (LC-HRMS) is a powerful tool. HRMS techniques, such as time of flight (TOF) or Orbitrap mass analyzers allow collecting full scan spectra with very accurate mass measurements and performing structural elucidations of unknown or suspected compounds [12,16,17]. In this work, a quadrupole-time-of-flight (Q-TOF) mass analyzer has been used for this purpose. Quadrupole allows the determination not only of the precursor ion but also of the product ions, providing information about fragmentation patterns and helping to the identification [18,19] of unknowns. Once the compounds were identified, visual comparison of chromatograms and principal component analysis of data allowed finding out migrants origin. The role of different composition of lacquers to avoid or delay migration is also discussed.

2. Material and methods

2.1. Reagents and solutions

Purified water was obtained with a Milli-Q 185 Plus system (Millipore, Bedford, MA, USA), and ethanol (HPLC quality) was purchased from ScharlauChemie S.A (Sentmenat, Spain). Methanol and water for UPLC-MS analysis (ultra LC-MS quality) were purchased from Baker (Deventer, The Netherlands). Standards were purchased for Sigma Aldrich Química (Barcelona, Spain).

2.2. Packaging materials

Fig. 1 shows the two different set of samples that were used in migration experiments, set A and set B.

Set A was composed by 5 different multilayer materials (1A, 2A, 3A, 4A and SCR1) manufactured using PET (polyethyleneterephtalathe), ink, adhesive, aluminum, gloss lacquer, matt lacquer and polyethylene. Set B was composed by 4 different multilayer materials (1B, 2B, 3B and SCR2), manufactured using OPP (oriented polypropylene), aluminum, adhesive, ink, paper, matt lacquer and polyethylene. In all the materials, polyethylene was the internal side of the packaging.

2.3. Migration tests

For migration test, pouches of 0.16 dm2 were manufactured by heat-sealing of the materials described in Fig. 1 (Set A: 1A, 2A, 3A, 4A and SCR1; Set B: 1B, 2B, 3B and SCR2).

Migration experiments were performed with 2 different simulants, ethanol 95% as fat simulant and Tenax® as dry foods simulant.

For ethanol experiments, pouches were filled with ethanol 95% according to the rate 6 dm^2 contact surface/kg of simulant established by the Regulation EU/10/2011 [20] and placed in the oven at 40 °C during 10 days. Afterwards, ethanolic samples were filtered through 0.20 μm PET filters and injected in the UPLC-QTOF-MS system.

For Tenax® migration experiments, pouches were filled with 0.64 g of Tenax® (4 g Tenax® per dm^2 laminate according to UNE-EN 14338 [21]) and placed in the oven at 40 °C during 10 days. Afterwards, Tenax® was extracted two consecutive times with acetone (5 g and 3 g respectively) in an ultrasonic bath for 1 h, following the methodology designed by Vera et al. [4]. The recovered acetone was filtered using PTFE filter (0.45 μm), concentrated under a stream of nitrogen up to 200 μL and finally injected in the UPLC-QTOF-MS system.

All the migration experiments were performed according to the European Regulation for food contact materials EU/10/2011 [20].

2.4. UPLC- QTOF-MS analysis

Chromatography was carried out in an Acquity system coupled with an ESCI probe to a Xevo G2 QTOF supplied by Waters (Milford, MA, USA). A UPLC BEH C18 column of 1.7 μm particle size (2.1 × 100 mm) also from Waters (Milford, MA, USA) was used. Injection volume was 10 μL. Chromatography was carried out at 0.4 mL min^{-1} column flow and 40 °C column temperature. The mobile phase was water with 0.1% formic acid (phase A) and methanol with 0.1% formic acid (phase B). Chromatography started at 98/2 phase A/phase B (1 min), changed to 0/100 in 6 min and stays at 0/100 during 2 more minutes. ESI probe and positive ionization were selected because of its capacity for ionizing most of the potential migrants. Instrumental parameters were as follows:positive ionization, sensitivity mode, capillary at 2.5 kV, extraction cone at 4 V, source temperature at 120 °C, desolvation temperature at 450 °C, cone gas flow at 20 L/hr, desolvation gas flow at 650 L/hr. Acquisition was carried out in MS^E mode, as this mode allows both, low and high, collision energies (CE) in the

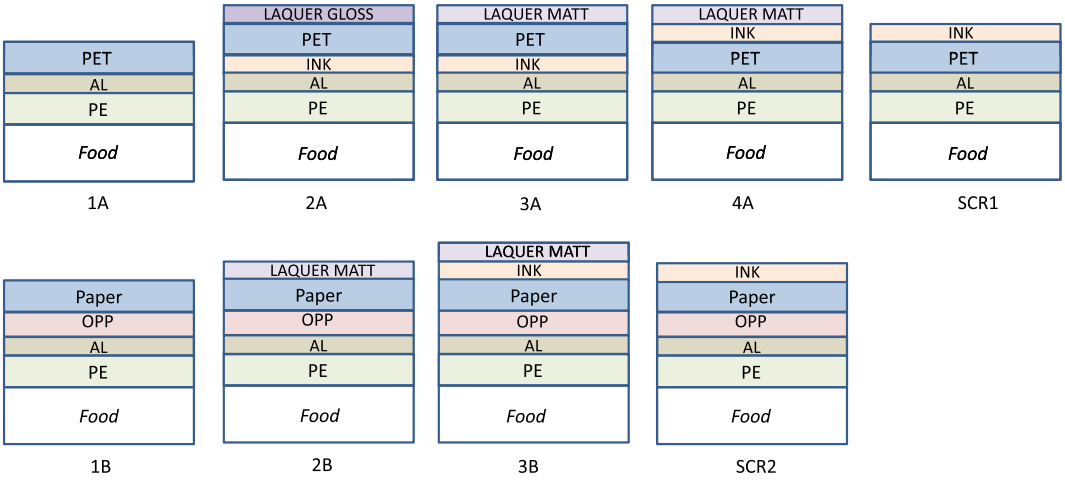

Fig. 1. Multilayer materials studied in set A and set B.