Talanta 191 (2019) 109–118

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Comprehensive analysis of photoinitiators and primary aromatic amines in food contact materials using liquid chromatography High-Resolution Mass Spectrometry

Yovana Sanchis[a], Clara Coscollà[a], Vicent Yusà[a,b,*]

[a] Public Health Laboratory of Valencia-FISABIO, 21, Avenida Catalunya, 46020 Valencia, Spain
[b] Analytical Chemistry Department, Universit of Valencia, Edifici Jeroni Muñoz, Dr. Moliner 50, 46100 Burjassot, Spain

ARTICLE INFO

Keywords:
High-Resolution Mass Spectrometry
Food packaging
Photoinitiators
Orbitrap
Primary aromatic amines

ABSTRACT

A comprehensive strategy for the analysis of UV-ink photoinitiators and primary aromatic amines (PAAS) in food-packaging materials such as, juice tetrabricks, pouches and bags has been developed using liquid chromatography coupled to Orbitrap High-Resolution Mass Spectrometry (LC-Orbitrap-HRMS). The methodology includes both quantitative target analysis and post-run target screening analysis. The quantitative method was validated after a previous optimisation of the single-stage Orbitrap fragmentation through the Higher-Energy Collisional Dissociation (HCD) Cell. Overall, the quantitative method presented recoveries ranging from 78% to 119%, with a precision (RSD) lower than 20%, for the 18 substances in the scope of the target method. Limit of quantification (LOQ) for UV-inks photoinitiators ranged from 0.5 $\mu g/kg^{-1}$ for Isopropyl Thioxanthone (ITX) and 2-Ethylhexyl 4-(dimethylamino) benzoate (EHDAB) to 5 $\mu g/kg^{-1}$ for the rest of photoinitiators. LOQ for PAAs were 2 $\mu g/kg^{-1}$ except for aniline (ANL) and 3,3′ dimethylbenzidine (3,3′-DMB) which was 2.5 $\mu g/kg^{-1}$ in the two studied simulants (acetic acid 3% and ethanol 50%). For post-run target screening a customized theoretical database, that included Bisphenols, Polyfluorinated compounds (PFCs), Phosphorus Flame Retardants (PFRs) and other substances was built. For identification purposes, a mass accuracy lower than 5 ppm, and some diagnostic ions including isotopes and/or fragments were used.

The strategy was applied to 18 samples collected in the Valencian region (Spain). No compounds were detected when the standardised migration test was applied. However, in the destructive test, benzophenone and EHDAB were determined from tetrabrick and pouch materials. In the post-run target analysis two PFCs (Perfluorooctanoic acid and Perfluoro-1-butanesulfonate) and four PFRs (2-ethylhexyl diphenyl phosphate, tris (2-choloroisopropyl) phosphate, triphenyl phosphate and 2-ethylhexyl diphenyl phosphate) were identified.

1. Introduction

There are hundreds of compounds that can migrate from food contact materials (FCMs). Some of them such as UV-ink photoinitiators and primary aromatic amines (PAAs) have similar physico-chemical characteristics and are prone to be analysed by similar analytical techniques.

UV-ink photoinitiators are commonly used in food-packaging materials and therefore, migration of ink components to food must be studied. Inks, defined as a coloured fluid or paste used for writing, drawing or printing, are mainly composed of a pigment or dye, suspended or dissolved in a solvent. Different groups of materials can be used in the manufacture of food packaging inks such as additives, colorants (pigments, dyes), pigment additives, polymeric resins, solvents or photoinitiators [1]. The presence of printing-ink components coming from food packaging has become a subject of concern since, in September 2005, the Rapid Alert System for Food and Feed (RASFF) published an alert from Italian authorities due to the detection of 2-ITX, a photoinitiator present in UV-cured inks, in baby milk [2]. The use of printing inks for food packaging is not regulated by European Regulations, and only exist some National Regulations guidelines.

The PAAs can migrate to foods from plastics such as kitchen utensils [3] or plastic laminates [4]. These amines are formed by hydrolysis of aromatic isocyanates in polyurethane adhesives [5]and by degradation of azodyes used as colorants in nylon kitchen utensils and other plastic materials. Brede et al. [6] identified the polyamide cooking utensils as a common source of PAAs. Some of the more relevant PAAs are: Aniline

---

* Corresponding author at: Public Health Laboratory of Valencia-FISABIO, 21, Avenida Catalunya, 46020 Valencia, Spain.
E-mail address: yusa_vic@gva.es (V. Yusà).

https://doi.org/10.1016/j.talanta.2018.08.047
Received 9 May 2018; Received in revised form 14 August 2018; Accepted 17 August 2018

(ANL), 4–4′ methylenedianiline (4,4′ MDA) and 4–4′ Oxidianilina (4,4′DPE) [3,4]. Regulation (EU) No. 10/2011[7] establishes that the specific migration limit (SML) for the sum of all the PAAs is 10 μg/kg.

The analysis of FCM contaminants can be performed in food, in food simulants or in food-contact materials. Migration on plastics intended to come into contact with food is regulated by Regulation (EU) No. 10/2011 [7]. The selection of simulants, such as ethanol and acetic acid, used in the present work are listed in the same regulation [7]. UV-ink photoinitiators and PAAs are polar compounds with low volatility and low thermal stability. LC–MS has been the selected technique in the analysis of photoinitiators and PAAs in plastic packaging [2,8–14] and plastic utensils [3,15] in the last years. Gallart-Ayala et al. reviewed [16] the analytical methods for FCMs using liquid chromatography until 2013. They concluded that MS/MS (QqQ) continues to be the method of choice in the analysis of food-packaging contaminants. Sanchis et al. included in their work LC-HRMS, a powerful analytical tool that allows the development of analytical strategies combining (i) target analysis (determination of specific priority analytes for which standards are available and for which accurate mass, retention time window, isotopic pattern and fragments are reliable identification tools); (ii) post-run target or retrospective screening analysis based on an accurate-mass customized database of known parent molecules and some diagnostic fragment ions or isotopic pattern, and (iii) non-target with no selection of analytes to be searched [9,17,18].

The LC-HRMS methodology using TOF or Orbitrap mass analysers has been recently introduced for the analysis of PAAs [3], inks [2], PFCs [19] additives [20] and phthalates [21] in FCMs. This technique has allowed the identification, in a non-target analysis, of Non Intentionally Added Substances (NIAS), unknown molecules possibly derived from polycarbonate degradation [19] and phthalates possibly derived from nylon kitchen utensils [3]. Mattarozzi et al. [4] developed a target methodology for the analysis of 22 PAAs from plastic laminates by LC–HRMS, with the LOQ ranging between 0.099 and 5.45 μg/kg [4]. LC–HRMS has also been used for the determination of PAAs from nylon kitchen utensils [3], achieving an LOQ of 2.5 μg/kg.

In some fields such as pesticide and veterinary drug analysis, this technique has increasingly become more popular [22,23] owing to its capacity of using the full-scan acquisition mode with high sensitivity, combined with high resolving power (> 50,000 FWHM) and accurate mass measurements (1–5 ppm).

In a previous published paper, in target analysis we have carried out an analytical method only for PAAs determination in nylon kitchen utensils [3]. In the present study we have developed a comprehensive analytical strategy including new important FCM contaminants in target analysis. These relevant compounds are the photoinitiators substances which are applied as an inks in commonly used food contact material matrices by adults and children. Our study is the first one which has developed and validated photoinitiators in food simulants by LC-HRMS.

Consequently, in this study we developed an analytical strategy that combines quantitative target analysis for UV-ink photoinitiators and PAAs with post-run target screening analysis (identification) based on a comprehensive customized database using LC-Orbitrap-HRMS. The analytical methodology was applied to plastic materials such as juice tetrabricks,pouches and bags samples collected in markets of the Valencian Region (Spain). To our knowledge, no work has previously reported analytical methods combining target/post-target analysis for photoinitiators and PAAs in the aforementioned plastic materials by liquid chromatography-high resolution mass spectrometry.

2. Experimental

2.1. Chemicals and reagents

For the target analysis, high-purity standard photoinitiators [1-hydroxycyclohexyl phenyl ketone 99% (HCPK), 2,2-dimethoxy-2-phenylacetophenone 98% (DMPA), 2,4-Diethyl-9H-thioxanthen-9-one 98% (DETX), 2-Ethylhexyl 4-dimethylamino-benzoate 98% (EHDAB), 2-Hydroxy-2-methylpropiophenone 99% (HMPP), Isopropyl Thioxanthone 99% (ITX), 4,4′-Bis-dimethylamino-benzophenone 98% (DEAB), 4-BenzoyIbiphenyl 98% (PBZ) and benzophenone 99% (BP)] and amines [2,6 Toluendiamine 98% (2,6 TDA), 2,4 Toluendiamine 98% (2,4 TDA), Aniline 98% (ANL), 1,5 Naphthalenediamine 99% (1,5 DAN), 1,3 Phenylenediamine 99% (m-PDA,) 4,4′diaminonaphenylether 98% (4,4′DPE) and 3,3′ dimethylbenzidine 98% (3,3′ DMB)] were supplied by Sigma Aldrich.

Individual stock standards were prepared by dissolving 25 mg of pure standard in methanol. Mix working solutions at 5 μg mL^{-1} were prepared with methanol. Two solutions at 100 ng mL^{-1} were prepared with acetic acid (AcH, 3%) and ethanol 50%, respectively. Calibration solutions from 0.4 to 160 ng mL^{-1} were prepared by adding variable volumes of the mix working solutions into two simulants (3% AcH in water, w/v) and (50% ethanol in water, w/v)

Regarding the post-run target analysis, all commercial standards of Phosphorus Flame Retardants (PFRs) 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-choloroisopropyl) phosphate (TCPP) and triphenyl phosphate (TPhP) were of high purity (> 95%) and were supplied by Dr. Ehrenstorfer (Ausburg, Germany) and Sigma-Aldrich (Barcelona, Spain). Standards of perfluoroalkyl substances (PFASs), Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS), were obtained from Wellington Laboratories (Guelp, ON, Canada) as methanol solutions at a nominal concentration of 50 μgmL-1. Each commercial standard of PFRs was weighed and dissolved in acetonitrile to obtain stock solutions of concentrations ranging from 2.0 to 4.0 mg mL^{-1}. For PFASs, individual stock solutions were prepared by diluting the commercial standard solution with acetonitrile to obtain 5.0 μg mL^{-1}. One of the individual mix working solutions was diluted with acetonitrile to obtain a concentration of 100 ng mL^{-1}.

Glacial acetic acid, ethanol absolute grade and methanol HPLC-M grade and Acetonitrile HPLC-MS grade were supplied by Merck (Darmstadt, Germany).

2.2. Sampling collection

A total of 18 plastic empty containers were provided by two food industries of the Valencian Region (Spain) during 2016: a) six Tetrabrick were destined to contain juice (with pH < 4.5) and juice with milk (with pH > 4.5); b) six pouches were destined to contain milk derivates, manufactured as infant food; and c) six bags to contain musts with fruit pulp (with pH > 4.5),

2.3. Sample preparation

Extraction of substances for the three studied materials was carried out in two different ways, standardised migration test (a) and destructive test (b).

(a) Standardised migration test

The migration test for the studied materials (bags, tetrabricks and pouches) was carried out following the European Union Regulation 10/2011. It is mandatory that this regulation be applied in plastic materials like bags cointaining musts with fruit pulp. Regarding pouches and tetrabrick materials, which are mainly made by multilayers, the regulation was applied because the inner layer was made of plastic.

Migration on tetrabricks and pouches was performed by filling them with simulant, because the internal part of the sample is destined to contain the food. Table 1 summarises the information about the simulant, the time and temperature applied in sample preparation for each matrix according to the Regulation 10/2011. Bags cointaining musts with fruit pulp were performed in steel stainless cells (Merck) where the inner layer was in contact with the simulant. In this case the layer