Journal of Chromatography A, 1372 (2014) 133–144

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Targeted and untargeted data-dependent experiments for characterization of polycarbonate food-contact plastics by ultra high performance chromatography coupled to quadrupole orbitrap tandem mass spectrometry

Chiara Bignardi, Antonella Cavazza, Claudio Corradini*, Paola Salvadeo

Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze 17/A, 43124, Parma, Italy

A R T I C L E   I N F O

Article history:
Received 3 September 2014
Received in revised form 24 October 2014
Accepted 27 October 2014
Available online 7 November 2014

Keywords:
Polycarbonate
Bisphenol A
Plastic additives
Organic colorants
High-resolution tandem mass spectrometry
Data-dependent acquisition
Food-contact material

A B S T R A C T

Materials that come in contact with foods are potential sources of chemical food contamination. Consequently, characterization of their composition is of paramount importance considering the possible occurrence of several unknown molecules such as non-intentionally added substance (NIAS), residual monomers, degradation products, plastic additives and organic colorants. Previous studies concerning the characterization in terms of composition are focalized in the recognition of additives. To the best author's knowledge there are no scientific data about the composition of a plastic material in terms of colorants.

In this work, an analytical method employing capillary ultra high-performance liquid chromatography and electrospray ionization quadrupole orbitrap high-resolution mass spectrometry (UHPLC–ESI Q-orbitrap) was exploited for characterization of polycarbonate for food contact material. Data-dependent experiments for targeted and untargeted analysis were employed after a total dissolution of polycarbonate samples and extraction of its components. The presence of common additives such as antioxidants and UV absorbers was confirmed by targeted analysis, while, the untargeted approach combined with the high mass accuracy of orbitrap technology allowed to identify for the first time some polycarbonate degradation products and the organic dyes effectively used for the coloration of plastic objects intended to come in contact with food. The present study shows the high potential of this technique in the field of material characterization aimed at food safety evaluation.

1. Introduction

Food contact materials are all materials and articles intended to come in contact with food, such as packaging and containers, kitchen equipment, cutlery and dishes. The safety of materials in contact with food must be evaluated since some molecules could migrate from materials into food. Materials should be manufactured in compliance with EU regulation, which also require good manufacturing practices, so that any potential transfer to foods does not raise safety concerns, change the composition of the food in an unacceptable way, or have adverse effects on the taste and odor of foods [1–3]. Plastic materials are composed by monomers and other starting substances transformed through chemical reactions in a polymer, which represents the principal component. Additives such as antioxidants, stabilizers and plasticizers have a major influence in the processing and shelf-life of plastics and are responsible for many properties of these materials. They are present in small amounts in plastics (generally ranging from 0.1% and 1%), dispersed in the polymer matrix, with the aim of avoiding effects such thermo-oxidative deterioration, which initiates scission and cross-linking of the macromolecular chains and consequently leads to polymer deterioration [4]. The polymer has got an inert structure with an high molecular weight that represents a low potential risk for human health since the organism cannot absorb molecules with a molecular weight greater than 1000 Da. On the contrary, as plastic additives and organic colorants have generally low molecular weight, they may migrate from plastics into foods, representing a potential risk for human health. Moreover, in polymer matrices it is possible to find monomers and oligomers that have not reacted in the polymerization reactions and non-intentionally added substances (NIAS) such as impurities of plastic additives [4].

* Corresponding author. Tel.: +39 0521 906023; fax: +39 0521 905557.
E-mail address: claudio.corradini@unipr.it (C. Corradini).

http://dx.doi.org/10.1016/j.chroma.2014.10.104
0021-9673/

Polycarbonate (PC) is one of the high-performance heterochain polymeric materials that comprise the family of engineering thermoplastics with a wide variety of applications due to excellent mechanical properties, high impact strength, heat resistance and high modulus of elasticity, as well as excellent toughness, clarity and transparency. These properties make it an ideal choice for tableware, microwave ovenware, reusable bottles, food storage containers and water pipes.

Bisphenol A is used as monomer for PC production, and it is considered to be an endocrine disrupter, as first reported in 1993 [5]. Recent studies indicate the potential of BPA to disrupt thyroid hormone action [6], cause proliferation of human prostate cancer cells [7] and block testosterone synthesis [8] at very low part-per-trillion doses. Use of BPA in food contact materials is permitted in the European Union (EU) under Regulation 10/2011/EU [3], although in January 2011, the European Commission adopted Directive 2011/8/EU [9], prohibiting its use for the manufacture of polycarbonate infant feeding bottles. The heightened interest in the safety of BPA used food contact applications has resulted in increased public awareness as well as scientific interest. Consequently, appropriate, reliable methodologies are crucial for both industrial and enforcement testing of compliance with the legislation, and for risk assessment [10,11]. Interest towards BPA gave rise to the development of many analytical methods with LODs low enough to assess the human exposure at low-dose [12], mainly carried out by gas or liquid chromatography coupled to fluorescent or UV detection, and mass spectrometry [13–18] aimed at its quantification in food simulants after migration tests [19–23] and also in real samples [24–26].

Nevertheless, apart from possible BPA release, PC contains additives and other low molecular weight compounds, which may represent potential migrating substances into food. In the last years, some analytical methods have been applied in the field of research on plastic additives. Two basic different approaches are pursued: one involving the extraction of additives from the polymer matrix followed by analysis; the second based upon their direct analysis within the intact polymer by ambient ionization mass spectrometry technologies, as very recently reviewed [27].

A number of papers employing HPLC–MS for the analysis of plastic additives in standard solution [28–33] and in real extracts [34–37] can be found in the recent literature. High attention has also lately been directed towards non-intentionally added substances (NIAS) possibly occurring. On the other hand, there is a lack of studies concerning the identification of organic colorants used in plastic materials intended to come in contact with food. Organic colorants are generally low-molecular weight compounds and, for this reason, represent, like additives, a potential risk for human health. Another important point is the identification of potential BPA-polycarbonate degradation products with molecular weight below 1000 Da, since the works present in literature are principally focused on the polycarbonate monomer and/or on its degradation products like 9′9-dimethylxanthene [14,20].

The present study reports a new analytical method developed by capillary ultra high-performance liquid chromatography (UHPLC) coupled to electrospray ionization high-resolution mass spectrometry (HRMS) employing the Q-exactive, a new benchtop mass spectrometer equipped with orbitrap technology, successfully applied in the field of proteomics [38,39] and drug discovery [40–44].

The high resolution mass spectrometry gives the advantages of unambiguously indentify a molecule thanks to the high mass accuracy, and this is crucial when unknown compounds have to be identified. A polymer extract is a very complex matrix and in this context, high resolution is decisive in the discrimination of very similar compounds, as for example oligomers derived from polymer scissions. The identification of the compounds of interest, such as plastic additives, NIAS, colorants and BPA-polycarbonate degradation products was achieved by performing targeted and untargeted experiments in both positive and negative ionization mode. This work shows some examples of data obtained by the application of this innovative technology in the detection of several classes of substances occurring in PC plastic materials, and demonstrates the applicability of the method to a possible useful survey for safety assessment.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical reagent grade. Methanol and water used as eluents were of UHPLC–MS grade and were purchased by Sigma Aldrich (Milan, Italy). Ammonium formate used as additive in eluents, chloroform, hexane and acetone was also purchased by Sigma Aldrich (Milan, Italy).

Pierce LTQ Velos ESI Positive ion and Pierce LTQ Velos ESI Negative ion calibration solutions from Thermo Fisher Scientific (Rockford, IL, USA) were used to calibrate the mass spectrometer.

The following compounds, which can be likely found in polycarbonate as monomers and additives, or degradation compounds, were selected: 2,2-bis(4-hydroxyphenyl)propane (BPA), BPA diglycidylether (BADGE), 2,2-Bis(4-hydroxyphenyl)propane-d_{16} (BPA-d_{16}), 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (Cyanox 2246), 2-hydroxy-4-methoxybenzophenone (Cyasorb UV9), 2,4-dihydroxybenzophenone (Uvinul 400), 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (Cyasorb UV12), 2,2′-dihydroxy-4-methoxybenzophenone (Cyasorb UV24), 2-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-2*H*-5-chlorobenzotriazole (Tinuvin 326), 2-hydroxy-4-*n*-octyloxybenzophenone (Chimassorb 81), 2-(2-hydroxy-3,5-di-*tert*-butylphenyl)-5-chlorobenzotriazole (Tinuvin 327), 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene (Irganox 1330), tris-(2,4-di-*tert*-butylphenyl)phosphate (Irgafos 168), 2-(2′-hydroxy-5′-*tert*-octylphenyl) benzotriazole (Cyasorb UV5411), octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Irganox 1076), 2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (Uvitex OB), 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (Tinuvin 234), 2-(2*H*-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (Tinuvin 328), 2,6-di-*tert*-butyl-4-methylphenol (BHT), butylated hydroxyanisole (BHA), 6,6′-di-*tert*-butyl-2,2′-thiodi-*p*-cresol (Irganox 1081), didodecyl 3,3′-thiodipropionate (Advastab 800) and pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate) (Irganox 1010) were purchased from Sigma Aldrich (Milan, Italy). Standard solutions of BPA, BADGE, Cyasorb UV 9, Cyasorb UV 12, Cyasorb UV 24 and Uvinul 400 at the concentration of 500 mg L^{-1} were prepared in methanol; all the other standard solutions at the same concentration were prepared in acetone.

2.2. Sample treatment and recovery

Four samples of PC tableware of different color (red, yellow, pink and orange) were investigated. The best procedure for cutting pieces of the samples to submit to extraction was optimized with the aim to avoid any thermal treatment. A hollow punch having a diameter of 25 mm was used to collect samples.

A crucial problem in the analysis of the compounds object of this study is that their molecules are inherently ubiquitous in the laboratory environment, and then could be introduced into the sample during sample treatment. Therefore, to preserve the sample solutions from any contamination due to possible contact with plastic material, all the laboratory procedures were performed employing