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An untargeted evaluation of the volatile and semi-volatile compounds migrating into food simulants from polypropylene food containers by comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry

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ABSTRACT

This study reports on the potential of comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC × GC − ToF MS) for the exhaustive untargeted characterization of the volatile and semi-volatile analytes migrating from four commercial polypropylene food containers into four simulants (water, 3% acetic acid, 10% ethanol, and isooctane) according to European Regulation 10/2011. Collected extracts were concentrated and directly subjected to GC × GC − ToF MS analysis without any further treatment to preserve migrants integrity. As expected, the nature and total number of compounds detected in the migrates depended on both the brand (i.e., manufacture and/or sterilization procedure) and the simulant applied. In total, 107 analytes, including some less volatile compounds, were either positively or tentatively identified in the investigated simulants, a number of these compounds being reported for the first time as migrants from this type of material. A database containing chromatographic, mass spectral and partition information concerning these compounds, plus 23 remaining unidentified, is provided.

1. Introduction

Food packaging materials made of plastic protect food against external pollution. However, these food contact materials (FCM) are not completely inert [1,2]. Apart from monomers, different types of additives, stabilizers, plasticizers or cross-linking agents are frequently added to plastics intended for FCM during the polymerization process to improve the properties and durability of the final packaging material. In the European Union (EU), only the substances included in the EU list of Regulation 10/2011/EU may be used in the manufacture of these FCM [3]. This list, that contains 885 substances and is regularly updated, also assigns specific migration limits (SML) to substances with potential to migrate into food at concentrations that may either endanger human health or promote an unacceptable change in food composition or a deterioration in its organoleptic characteristics. However, despite these regulation actions, many studies have repeatedly reported on the capability of some of these additives and other components to migrate from plastic containers into food and food simulants [1,4–6]. Migrating compounds include, among others, decomposition products, reaction and intermediate products, and other non-intentionally added substances (NIAS); but also compounds generated during the subsequent plastic sterilization processes [4,7,8]. The nature of these migrating substances cannot be predicted from the starting substances due to the possible presence of unknown by-products and/or neo-formed compounds not previously described [2,9]. In addition, the real composition of the different ingredients and materials used to manufacture the plastics is not always fully declared (or known) by plastic producers [10]. Therefore, in practice, a realistic chemical characterization of the substances migrating from FCM into food can only be accomplished by developing migration experiments. For such an experiments, the use of simulant solutions is recommended by Regulation 10/2011/EU due to the inherent complexity of most foodstuffs [3,11].

It can be anticipated that an increasing number of non-identified compounds and NIAS will be detected in future in migration studies due to the use of increasingly powerful analytical techniques [2,4,9,12]. Up to now, in most instances, the identification of these minor components have relied upon the use of powerful mass spectrometry- (MS-)based detectors with high identification capabilities (i.e., high and ultra-high

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resolution MS) [2,6,9,11,12]. However, somehow surprisingly, the use of also powerful separation-plus-detection techniques, such as comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC × GC − ToF MS), in this field has been much more limited and, in general, orientated to the characterization of preselected groups of compounds [10] or the impurities or break-down products of specific plastic components [1,4,13]. To our knowledge, no study on the potential of GC × GC − ToF MS for the untargeted characterization of migrates obtained by treating plastic food containers with selected food simulant solutions has been reported by now in the literature. Therefore, the aim of this study was to evaluate the feasibility of GC × GC − ToF MS for the exhaustive characterization of the volatile and semi-volatile compounds present in the extracts obtained when exposing four commercial polypropylene food containers to selected food simulants, i.e. water, aqueous solutions containing 3% (w/v) acetic acid and 10% (v/v) ethanol, and isooctane, at 40 °C for 10 days. Under these conditions, the overall migration under long term storage at room temperature or below, and short heating were tested. From these data, a database containing chromatographic, mass spectral and partitioning information of both identified compounds and those remaining as unknown was created to assist other authors in their future studies concerning the identification of migrants from this type of plastic material.

2. Materials and methods

2.1. Reagents and samples

Acetic acid, ethanol and isooctane were for residue analysis and acquired from Merck (Darmstadt, Germany). Anhydride sodium sulfate was from Panreac (Barcelona, Spain). Milli-Q water was obtained from a Millipore system unit (Bedford, MA, USA). A number of micro-contaminants, including phthalates, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybromo biphenyl ethers (PBDEs), isomers of dechlorane plus (DP) and organophosphorus flame retardant standards were available and used for analyte positive confirmation. (The reader is referred to the Supplementary Data-1 section for additional details concerning the pure standards used in the study.)

The 250 mL polypropylene food storage containers identified as authorized FCM according to current legislation [14] and intended for domestic use were acquired in local retail markets in Madrid (Spain). They belonged to different brands (identified throughout the study as A, B and C). According with their respective labels, food storage containers A and B were manufactured in the EU, while C was manufactured outside the EU. All containers offered a translucent appearance and were commercialized as appropriate for food storage at refrigerated and frozen conditions (down to − 40 °C for brand A and down to − 25 °C for brand C) and for microwave heating (up to 120 °C brand A and up to 90 °C brand C). No usage temperature range was specified in the case of brand B. Usage recommendations were reported in a small sticker stuck in the outside front for food containers from brands A, B and C, while the container from brand B was surrounded by a (apparently non-recycled) paperboard.

The fourth investigated polypropylene food storage container was a one piece disposable plastic box used to transport and deliver prepared food. In principle, it had similar characteristics to the previously described food containers selected for the study. No usage temperature range was specified on this food container. The container was commercialized without stickers or paperboards. This food container was identified as brand D through the study. All food containers were simultaneously acquired and maintained in a laboratory cupboard preserved from light until analysis.

2.2. Migration experiments

Distilled water, aqueous solutions containing 3% (w/v) acetic acid (simulant B) and 10% (v/v) ethanol (simulant A), and isooctane (simulant D2) representing, respectively, aqueous, acidic, alcohol-containing and fat-containing foods according to Regulation 10/2011/EU [3], were used as food simulants. These migration solutions were identified, respectively, as simulants S.1 to S.4 throughout this study. The mentioned European Regulation stipulates that, in migration tests, food containers should be placed in contact with the selected food simulants at the worst conditions of temperature and contact time. This study intended to evaluate the overall migration under long term storage conditions at room temperature or below, or short heating conditions. Thereby, according to the European Regulation, the migration tests were performed by treating the food containers with the corresponding food simulant at 40 °C for 10 days (test OM2 as described in Regulation 10/2011/EU) [3].

In a typical migration test, the four investigated food containers, pre-washed with Milli-Q water and air-dried, were filled up to three quarts of their capacity (i.e., 200 mL) with the corresponding simulants and kept in the dark, closed, at 40 °C for 10 days in a drying oven (Nahita, model 631/6; Madrid, Spain). Apart from the four investigated containers, each migration test included a reagent blank (i.e., 200 mL of the evaluated simulant placed in a closed glass Erlenmeyer flask), which was subjected to the same treatment. Once the incubation period was completed, the simulant was removed, the container was rinsed with Milli-Q water, air dried and treated with another food simulant in an attempt to obtained some extra information on the relative extraction capabilities of the four evaluated simulants while promoting a sequential reduction of the complexity of the migrants mixtures. Simulants were always applied following this order: (1) water, (2) 3% acetic acid, (3) 10% ethanol, and (4) isooctane. The collected simulant extracts were slowly concentrated in a rotary evaporator with careful temperature and pressure control. The final volume adjusted to 100 μL under a gentle nitrogen stream to minimize the possible losses of the most volatile migrants. Aqueous simulants were reconstituted in acetone and dried with sodium sulfate before instrumental analysis. Meanwhile, no solvent exchange was performed in the case of the isooctane extracts. The use of plastic materials was minimized during the whole sample treatment (e.g., the use of gloves was avoided) to avoid cross contamination, in particular from plasticizers. Glassware material was heated in a muffle furnace (6 h at 400 °C) and, then, sequentially rinsed with Milli-Q water, methanol, acetone, dichloromethane and *n*-hexane and protected with aluminum foil until use.

Otherwise specified, experiments were done in duplicate, i.e. two complete independent series of food containers were subsequently treated with the selected simulants, yielding a total of 32 extracts and 8 reagent blanks. No significant interference was introduced by the applied analytical procedure, except for some specific phthalates whose presence in the migrates was corrected as explained below.

2.3. Instrumental analysis

The GC × GC − ToF MS analyses were performed on a Pegasus 4D (Leco Corp., St. Joseph, MI, USA). The instrument consisted of a modified Agilent 6890 GC coupled to a ToF MS and equipped with a split/splitless injector. Samples were injected in the hot splitless mode (1 μL at 275 °C, 2 min) into a column set consisting of an HT-8 (30 m × 0.25 mm *i.d.*; 0.25 μm film thickness; 8% phenyl (equiv.) polycarborane siloxane) as first dimension column coupled to a BPX-50 (1.7 m × 0.1 mm *i.d.*; 0.1 μm film thickness; 50% phenyl 50% methylpolysilphenylene siloxane) as second dimension column. Both columns were purchased from SGE (Melbourne, Australia). The column set and initial experimental conditions were selected on the base of our previous experience in the analysis of complex mixtures [15,16], although reoptimised to avoid coelution among the target compounds and among these and the co-extracted matrix components. Once optimized, the temperature of the main oven was programmed from 45 °C [60 °C in the case of the isooctane extracts] (2.5 min) to 190 °C at a rate of 20 °C/min

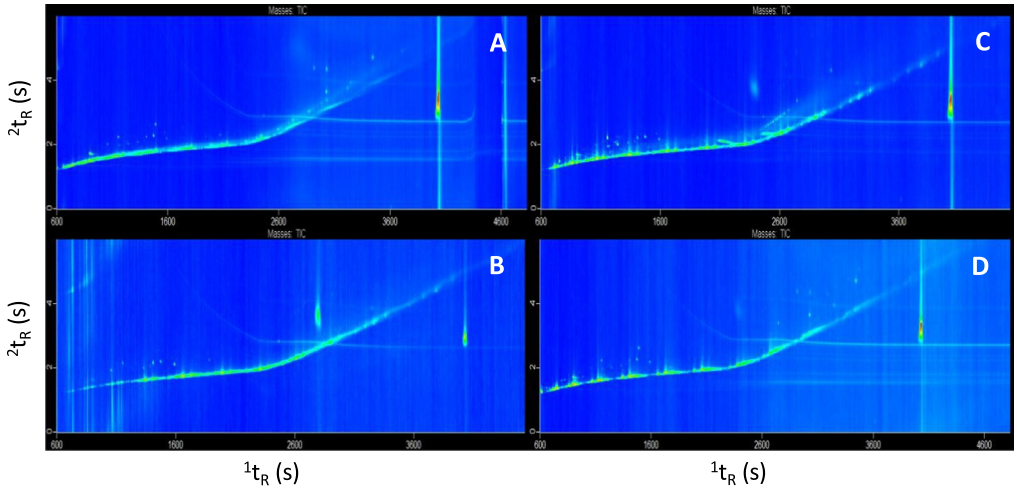

Fig. 1. Comparison of the two-dimensional total ion current (TIC) chromatograms obtained after treatment of the investigated food containers with isooctane. Panel letters agree with those assigned to food containers brands.

and then to 300 °C (30 min; 35 min in the case of the isooctane extracts) at 3 °C/min. The second dimension oven was programmed to track the main oven but with an off-set of 30 °C, except for the final temperature, i.e. 75 °C [90 °C in the case of the isooctane extracts] (2.5 min) to 210 °C at a rate of 20 °C/min and then, at 3 °C/min, to 300 °C (kept constant until the end of the chromatographic run). Helium was used as carrier gas at a head-column pressure of 30 psi, which was maintained constant through the whole analysis. A nitrogen quad-jet dual-stage cryogenic modulator was used. The temperature of the modulator was set 40 °C above that of the main oven. A modulation period of 6 s with a 0.6 s hot jet pulse was used. The transfer line temperature was set at 275 °C.

The ion source temperature was set at 250 °C. Total ion monitoring was performed in the *m/z* 75–700 range; the energy of ionizing electrons was 70 eV and the voltage of the multiplier was 1670 V. The acquisition rate was set at 100 Hz in all instances. ChromaToF 4.2 was used for data acquisition and treatment. This software allowed automated baseline correction, peak deconvolution, and peak area and volume determination. The minimum required signal/noise (S/N) ratio for each detected peak was set at 100 to ensure proper recognition and integration of analytes present in the extracts at the ppm-ppb level while preventing the unnecessary integration of a large number of matrix components present at concentrations close to background level. A script function written in Visual Basic was used for automatic data filtering and identification of halogen-containing compounds on the base of characteristic *m/z* ions and clusters [15]. Several identification levels were differentiated during the analysis [2]. When authentic standard was available, positive identification of the peak detected in a sample was based on the mutual agreement of the retention time and mass spectrum with that of the corresponding standard analyzed under identical experimental conditions. When an appropriate standard was not available, the tentative identification of the detected compound was based on the following multi-criteria approach [15]: (i) individual (i.e., manual) confirmation of preliminary assignment done by automatic peak finding by the software (minimum spectra similarity score, 750); (ii) identification of potential isomers belonging to the same class on the base of mass spectrum similarity with analytes positively identified and their clustering within the structured chromatograms generated by the column set used in the present study; (iii) positive match of the distribution patterns of the mass spectrum (*m/z* ratios) and positive comparison with those of commercial libraries and/or described in the literature; and (iv) mass spectrum interpretation.

The limits of detections (LODs) of the proposed methodology was evaluated for the pure standards and determined to lay, in general, in low $\mu g\,L^{-1}$ range, corresponding to LODs of 4 $\mu g\,Kg^{-1}$ or lower for intermediate to low volatility compounds (in the 14–75 $\mu g\,Kg^{-1}$ range for the less volatile analytes detected in the investigated migrates) [15,17]. These LODs were considered to allow proper detection of the analytes present in the migrates at levels below the thresholds set in current regulation [3].

3. Results and discussion

3.1. General overview

A preliminary inspection of the two-dimensional chromatograms (contour-plots) obtained by GC × GC − ToF MS analysis of the migrates from the studied food containers demonstrated that analytes with widely divergent volatilities and polarity were found in the four fractions investigated. The former spread out in the first dimension, while the latter spread out in the second dimension. More importantly, these analytes showed an appropriate separation from other co-extracted matrix components eluting at the bottom of the contour-plot, a result that illustrated the adequacy of the selected column set and the applied experimental conditions for the intended analyses. As somehow anticipated, differences were observed among the chromatograms obtained from the same food container depending on the nature of the simulant applied (see Supplementary Data-1 Fig. S.1). Furthermore, although the same polymer was used to produce all studied containers, significant differences existed also among the chromatograms obtained for the same simulant depending on the food container analyzed (see Fig. 1 for a typical example). This observation agreed with previous findings reporting on the influence of the manufacturing procedure on the number, concentration and nature of the migrants detected in the simulant extracts [6,10]. All together evidenced the difficulties associated to this type of determinations and the utility of untargeted analyses in order to have a more realistic evaluation of the migration process.

In general, the simulants extracting the largest numbers of analytes from the investigated food containers were 10% ethanol (S.3) and isooctane (S.4). Among the investigated food containers, the ones showing the largest number of migrants were brands A and D, followed by brands C and B. The total number of identified compounds for these food containers (under the proposed analytical and data processing conditions) ranged between 102 (for brand A; 100 for brand D) and 54 (brand B). [Note that already well-characterized monomers and related compounds, saturated hydrocarbons and other low molecular weight analytes thoroughly reported in the literature were not considered in the present study [4,18–20]. This general overview can also be read out from Table S.1, where information concerning the most relevant analytes detected in the migrates obtained by treatment of the investigated

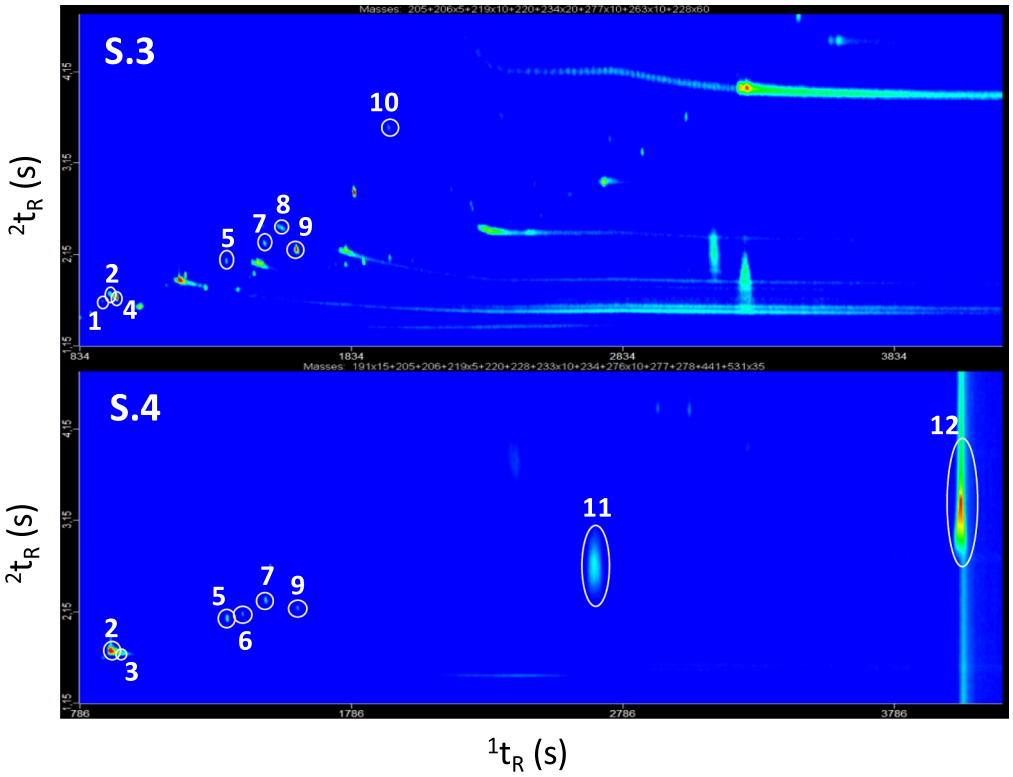

Fig. 2. Main antioxidants and breakdown products identified in the ethanol (S.3) and isooctane (S.4) lixiviates obtained from food container D. Peak numbering: (1) 2,4-di-*tert*-butylphenol isomer; (2) 2,4-di-*tert*-butylphenol; (3) 2,6-di-*tert*-butylbenzoquinone; (4) butylated hydroxytoluene; (5) 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde; (6) 3,5-di-*tert*-butyl-4-hydroxyacetophenone; (7) methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate; (8) 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid; (9) 7,9-di-*t*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione; (10) bisphenol A; (11) Irganox 1076; and (12) Irgaphos 168. *m/z* values used to reconstruct the chromatograms: 191 × 15, 205, 206, 219 × 5, 220, 228, 233 × 10, 234, 276 × 10, 277, 278, 441, 531 × 25.

food containers with the four assayed simulants is summarized. In total, 107 migrants were either positively or tentatively identified in the studied extracts, while 23 analytes remain as *unknowns*. The complete list is also presented in Supplementary Data-2 as a searchable table, where analytes have been sorted according to their first dimension retention time. For the sake of comparison, all analytes retention times have been referred to those obtained for the isooctane extracts in the first dimension. Only analytes showing an abundance ten times higher than that of the corresponding compound in the reagent blank (when detected) have been considered as positive in the samples and included in this table. (Note: it should be mentioned that, in the investigated migrantes, this consideration applied essentially for phthalates.) The most characteristic *m/z* values for each compound are also mentioned.

The presence of migrating chemicals, and in particular NIAS, in these extracts is discussed in following sections according to the most probable source of the analytes.

3.2. Identification of compounds present in the migration solutions

3.2.1. Antioxidants and their breakdown products

Some of the most frequently detected NIAS in simulant studies are either impurities (including by-products) introduced during the synthesis of the plastic material or breakdown products. The later are associated to degradation processes, which can affect the polymer itself or some of the additives included in the formulation to improve the physico-chemical properties of the final material. The main degradation pathways are the exposure of the polymer to high temperatures or high irradiation energies [2,4]. These processes can occur during the manufacture of the polymer (e.g., during thermal-mechanical processes), or as consequence of the exposure of the plastic to microwaves [7] or irradiation for sterilization purposes [4,21]. The analytes resulting from these degradation processes are typically molecules with a molecular weight lower than the original compound and, consequently, with a greater potential to migrate from the polymer. However, some of these processes have also been reported to generate heavier oxidation products with capacity to migrate from the polymer [21].

The antioxidant Irgaphos 168 [tris(2,4-di-*tert*-buthylphenyl)phosphite] is an accepted additive for polymers [3]. Because of its recognized capability to migrate from plastic, the EU set a specific migration limit (SML) for this compound of 60 mg kg^{-1}. However, current legislation did not set any type of SML for their two known degradation products, 2,4-di-*tert*-butylphenol and tris(2,4-di-*tert*-buthylphenyl) phosphate [21]. Irgaphos 168 and its oxidized degradation product were clearly detected in the isooctane extracts obtained from the four food containers investigated. Meanwhile, 2,4-di-*tert*-butylphenol was detected in all studied migrates, with the only exception of those obtained by treatment of food container B with 3% acetic acid and 10% ethanol. In addition, an isomer of this compound was also found in food containers A, C and D, in particular in the alcoholic extract.

Another antioxidant, Irganox 1076 (octadecyl 3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate), was detected in the isooctane fraction obtained from container D [22]. The presence of methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, a compound identified as product of degradation of Irganox 1076 and/or Irganox 1010 [5] in this lixiviate for all studied containers, would suggest that these antioxidants could have been included in the formulation of the investigated polypropylene materials. The simultaneous presence in other extracts of compounds considered degradation products of these Irganox derivatives, such as 2,6-di-*tert*-butylbenzoquinone (isooctane fraction of brands C and D) and 7,9-di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (distributed in different fractions with the exception of water) [5,23], would contribute to support the previous statement.

2,6-Di-*tert*-butyl-4-ethyl-phenol is an antioxidant used in plastics and rubber products to improve their temperature stability and discoloration resistance [24]. This compound was only detected in the isooctane fraction of food container A, a partition behavior that could be associated to the hindered structure of this phenol. Another frequently used phenolic antioxidant, butylated hydroxytoluene, was detected in the acidic and alcoholic migrates from all investigated brands, while its transformation product, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, was mainly found in the isooctane extracts. The position of this compound in the contour plot (retention times: 1332,

2.10) is shown in Fig. 2, where it is identified as peak number 5. This figure shows also the position of other relevant antioxidants and some of their breakdown products identified in lixiviates from food container D.

3.2.2. Plasticizers

Bis-(2-ethylhexyl) phthalate is one of the most commonly applied plasticizers in plastic products. Its use in FCM is limited in current legislations (1.5 mg kg^{-1}) [3] and, to protect human health, the European Food Safety Authority (EFSA) established a total daily intake for this compound of 0.05 mg kg^{-1} body weight [25]. This compound was positively identified in the acidic, ethanoic and isooctane migrates of nearly all containers. Different compounds have been identified as metabolites of bis-(2-ethylhexyl) phthalate (e.g., 2-ethylhexanoic acid, 2-ethylhexanol, phthalic acid, mono-2-ethylhexyl phthalate) [26], and consequently suggested as possible degradation products of this phthalate [1]. However, none of these compounds were detected in the analyzed migrant solutions.

Dibutyl phthalate is another plasticizer frequently detected in plastic materials [5]. Although its SML is even more restrictive than that of di-(2-ethylhexyl) phthalate (0.3 mg kg^{-1}) [3], this compound was positively identified in nearly all the analyzed migrates (the only exception was the ethanoic one obtained from brand container B). In addition, an isomer of this phthalate was also detected in the ethanol and the acid migrates from brand containers A and C, respectively.

Other phthalates with a high detection frequency in the investigated migration extracts were the diethyl phthalate and the diisobutyl phthalate, which were detected in all analyzed solutions. No legal SMLs have been set in current EU legislation for these chemicals.

3.2.3. Cross-linking agents

2-Mercaptobenzothiazole is incorporated during the manufacture of plastics in small amounts to aid during the vulcanization process. However, this compound, which was only detected in the water extract from food container A, can also be formed by degradation of other additives (e.g., by hydrolysis of the accelerator N-(1,1-dimethylethyl)-2-benzothiazolesulfenamide) [24]. Benzothiazole, which was identified in the alcoholic solutions of brand containers A and C and in all water extracts obtained from brand container D, is another by-product frequently detected in plastic migration studies [27–29].

Retarders are chemicals added to slow down the crosslinking process. Commonly used retarders include stearic acid, salicylic acid, benzoic acid and phthalic anhydride. The two latter compounds were detected in the investigated migrates. Both compounds were found to migrate into water and, to a lesser extent in the case of the phthalic anhydride, into the 3% acetic acid simulant (Table S.1).

3.2.4. Other additives

N,N-bis-(2-hydroxyethyl)alkyl(C13-C15) amine is an additive used as antistatic agent during the manufacture of polypropylene [24,30] and with a legislated SML of 1.2 mg Kg^{-1} (expressed as tertiary amine). Up to 19 possible degradation products associated to this mixture of compounds were tentatively identified in this study (compounds named as N,N-bis-(2-hydroxyethyl)alkyl amine related in Table S.1). These compounds were found, in particular, in the water and ethanol simulants of containers A and D, where they were detected as intense peaks with a severe tailing in the first chromatographic dimension evidencing analyte degradation in the injector and/or in the first dimension column [31] (see Fig. S.2 for a typical example). The number of compounds of this dihydroxy alkyl amine family detected in the present study were higher than those identified by Vera et al. [6] on polypropylene films. In that recent study, the authors reported on the presence of 10 N,N-bis-(2-hydroxyethyl) C8-C22 amine related compounds, although in that case liquid chromatography with high resolution MS detection was used for the analysis. A number of these chemicals was also previously identified by Bradley and Coulier [1], who suggested that they are formed by thermolysis of the parent additive.

Glycerol monostearate is a non-ionic surfactant authorized as external lubricant for plastics [3]. This compound is obtained by reaction of triglycerides with an excess of glycerol. Consequently, expected impurities include diglycerides, unreacted triglycerides, glycerol and fatty acids (i.e., stearic acid, tetradecanoic acid, hexadecanoic acid) and their esters. Glycerol monostearate was not found in the investigated extracts. However, up to seven compounds associated to this chemical (named as glycerol monostearate related in Table S.1) were tentatively identified in all aqueous migration solutions obtained from containers A, C and D. Nevertheless, it must be accepted that two of these compounds (those eluting at retention times in the first dimension of 1968 and 2286 s) could also be breakdown products of glycerol monooleate, another non-ionic surfactant and emulsifier accepted for plastic manufacturing. Some of the acids (i.e., even acids from dodecanoic to octadecanoic acid) and their corresponding esters detected in the different migrates could be breakdown products of these glycerols. Nevertheless, some of these compounds are also used as additives (mainly lubricants or heat stabilizers) during plastic manufacturing. The presence of some of these analytes and their alkylated derivatives has been previously reported in polypropylene intended for food contact [1,5], while only a very recent reference reporting on the presence of the previously indicated glycerol related compounds in these FCM has been found in the literature [6].

Oleamide is an amide derived from the oleic acid, whose use is accepted as lubricant during plastics production [3]. Oleamide was tentatively identified in the acidic and alcoholic simulants obtained from containers C and D, a result that agreed with previous observations [32]. Interesting, several compounds related to this fatty acid (i.e., hexadecenamide, hexadecanamide and octadecanamide) were also detected in these extracts. Other less frequently used additives [30], such as erucamide [4,32], were not detected in the investigated migrates under the applied analytical and data processing conditions.

3.2.5. Contaminants

Recycling of the plastic materials has dealt in certain occasions to contamination of the new products with chemical compounds coming from the previous packages or from the misuse of these packages by consumers before they were discarded [5,20,22,33]. In other cases, contaminants have been associated to the use of printing inks, paperboards, adhesives or substances added to color the final material [2,34]. The food containers evaluated in this study were translucent and colorless. They did not have any type of printout, but containers A, B and C had a small sticker stuck in the outside front; food container B was also surrounded by a (apparently non-recycled) printed paperboard.

Naphthalene is an often detected compound in polypropylene food containers [5]. Some of its alkyl-derivatives, in particular 2-methylnaphthalene and 2,6-dimethylnaphthalene, have also been detected in plastic containers made with different plastic materials, although their presence in polypropylene-based products is apparently less frequent [5]. In the food containers investigated in this study, apart from naphthalene, up to 13 alkylated naphthalene derivatives were detected (Table S.1). These derivatives included two C1-naphthalenes (i.e., methyl-naphthalenes), three C2-, one C3- and seven C6-naphthalene derivatives. Among the later, it was possible to differentiate the trimethylpropenyl-naphthalenes from other diisopropyl-isomers on the base of their respective mass spectra (main fragments were obtained at m/z of 195 and 210 for the former, while the main fragments were at m/z 197 and 212 for the later) and their different position in the contour plot (Fig. S.3). In general, most of these compounds were found in the isooctane fraction, a finding consistent with their non-polar nature. The isooctane migrates containing more alkyl-naphthalenes were those obtained from food containers C and A. The presence of diisopropylnaphthalene has been reported in some migration studies involving plastic bottles and other plastic articles, including those made from

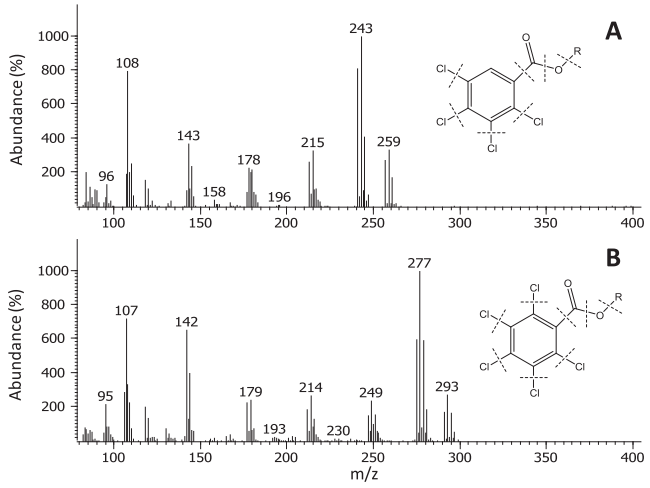

Fig. 3. Mass spectra of two unknown analytes containing (A) four and (B) five chlorines in their structure as detected in the ethanol lixiviate of food container C and proposed molecular structures.

propylene. The presence of this chemical, not regulated for plastics, has been associated with a possible migration from inks in the papers and boards reporting the brand and instruction of the food container [2,34]. The simultaneous presence of benzophenone (also use for this purpose) in the isooctane migrates would contribute to support this idea.

Apart from this naphthalene-series, three other regulated PAHs were detected in the isooctane extracts, acenaphthene (in food container C), fluorene (in containers from brands A, C and D) and phenanthrene (in the four investigated containers). To our knowledge, none of these heavier PAHs have been previously detected in migrates from polypropylene food containers.

The application of a script function previously developed in our group for the automatic filtering and identification of halogen-containing chemicals [15] confirmed that only a very limited number of analytes with these characteristics were present in the investigated migrates. Xenobiotics like PCBs, PBDEs or DP isomers were not present in the analyzed extracts, although these microcontaminants have been detected in some recycled plastic materials [24,35]. However, three other compounds containing chlorines were detected in some of the analyzed ethanoic fractions. Two non-identified chlorinated compounds were present in the ethanol extracts from brand A (compounds identified as Unknown 2 and 3 in Table S.1). The isotopic clusters observed in the mass spectra of these compounds suggested a tetra- and penta-chloro substitution in their molecules, respectively (Fig. 3). Meanwhile, the similar fragmentation pathways and the coincidence of the several *m/z* fragments observed in both cases would suggest a tetra- and penta-chlorinated benzoate-related structure for both analytes (Fig. 3). To our knowledge, no reference reporting on the presence of this type of analytes in FCM can be found in the literature. Apart from these two chlorinated compounds, one organophosphorous flame retardant, tentatively identified as tris(2-chloroisopropyl)-phosphate, was also detected in these extracts in all investigated food containers.

The mass spectra of other non-identified compounds present in the investigated extracts are shown as part of the Supplementary Data-3. It is interesting to mention that, on the base of these mass spectra, it can be suggested that 10 out of the 21 compounds remaining as unknown in these samples (i.e., analytes identified as Unknown 4–11, 13 and 18 in Table S.1) could belong to the same chemical class.

4. Conclusions

This study illustrated the potential of the combined enhanced separation power and sensitivity (in general, in the low μg Kg^{-1} level) provided by GCxGC, and the identification capabilities derived from its hyphenation with ToF MS for the non-orientated characterization of semi-volatile and volatile compounds migrating from commercial polypropylene food containers subjected to migration tests according to current EU legislation. Although well-characterized monomers and related compounds, saturated hydrocarbons and certain thoroughly described volatile analytes were excluded from discussion, a total of 107 migrants were either positively or tentatively identified in the four investigated simulants (water, 3% acetic acid, 10% ethanol and isooctane) under the analytical and data processing conditions applied. Other 23 compounds remained as unidentified. A large majority of the identified compounds were NIAS and, interestingly, some of them showed a limited volatility. These findings demonstrated the complexity of this type of determination and justified the requirement of using analytical techniques providing improved separation and/or detection capabilities. Identified NIAS came from degradation or reaction of allowed additives, but they can also be impurities of these or other added chemicals. Several of these NIAS have been identified for the first time in this type of material. Data concerning the chromatographic and migration behavior as well as the mass spectrometric data of detected migrants have been summarized and organized in a searchable database to be used by other researchers involved in this type of analysis as support for their identifications. Nevertheless, more work in this field is still desirable in order to complete uncovered information regarding the potential presence in the migrates of other polar and non-volatile analytes not amenable by the proposed gas chromatography-based methodology.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.12.011

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