Identification of substances migrating from plastic baby bottles using a combination of low-resolution and high-resolution mass spectrometric analysers coupled to gas and liquid chromatography

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Abstract

This work presents a strategy for elucidation of unknown migrants from plastic food contact materials (baby bottles) using a combination of analytical techniques in an untargeted approach. First, gas chromatography (GC) coupled to mass spectrometry (MS) in electron ionization (EI) mode was used to identify migrants through spectral library matching. When no acceptable match was obtained, a second analysis by GC-(EI) high resolution mass spectrometry (HRMS) time-of-flight (TOF) was applied to obtain accurate mass fragmentation spectra and isotopic patterns. Databases were then searched to find a possible elemental composition for the unknown compounds. Finally, a GC hybrid quadrupole QTOF-MS with an atmospheric pressure chemical ionization (APCI) source was used to obtain the molecular ion or the protonated molecule. Accurate mass data also provided additional information on the fragmentation behaviour as two acquisition functions with different collision energies were available (MS^E approach). In the low energy (LE) function, limited fragmentation took place, whereas for the high energy (HE) function, fragmentation was enhanced. For less volatile unknowns, ultra-high pressure liquid chromatography (UHPLC)-QTOF-MS was additionally applied. Using a home-made database containing common migrating compounds and plastic additives, tentative identification was made for several positive findings based on accurate mass of the (de)protonated molecule, product ion fragments and characteristic isotopic ions. Six illustrative examples are shown to demonstrate the modus operandi and the difficulties encountered during identification. The combination of these techniques was proven to be a powerful tool for the elucidation of unknown migrating compounds from plastic baby bottles.

Keywords: Baby bottles; migration; GC-(Q)TOF-MS; UHPLC-QTOF-MS; food contact materials

Introduction

Nowadays, there is an increasing concern over the presence of hazardous chemicals in food contact materials (FCMs) [1,2]. Many of these FCMs are made of plastics, which, next to the polymer, contain complex mixtures of compounds, such as monomers, additives, catalysts or degradation products. Consequently, migration of these chemicals from the plastic FCMs into the food could arise, resulting in off-flavours and taints in the food or even harmful effects to human health. For plastic FCMs, all authorized starting substances have been assembled in a Union List in EU Regulation 10/2011 together with their migration limit and/or restricted use. [3]. Furthermore, the use of Bisphenol-A was banned for the manufacture of polycarbonate (PC) infant feeding bottles and their placement on the European market. [4]. As a consequence, baby bottles made of other polymer types, e.g. polypropylene (PP) or polyamide (PA), are now present on the market.

The migration phenomenon in the alternative materials for baby bottles has been understudied up to now and little is known about the possible migrants from these polymer alternatives. GC quadrupole-MS (GC-Q-MS) with electron impact (EI) ionization source has been used to investigate the presence of unknown compounds in food simulant that has been in contact with the alternative baby bottle plastics [5,6]. The drawback of this approach is that a conclusive library match cannot always be obtained when comparing experimental and library EI spectra, as many migrating compounds can be new, unregulated, or even non-intentionally added substances (NIAS); e.g. degradation products of polymerisation reaction, and are thus not included in commercially available libraries.

Using high-resolution time-of-flight mass spectrometry (TOF-MS), the identification process improves as accurate masses of the ions are obtained. Moreover, the sensitivity is notably higher than of the quadrupole MS when working in full-spectrum acquisition. The compounds tentatively identified by library matching can be confirmed by checking the accurate-masses of the product ions and the molecular ion (if present in the EI spectrum) and ambiguous results in the library search can be partly resolved [7]. Only recently, such accurate-mass instruments have also been coupled to alternative (softer) ionization sources for GC, e.g. atmospheric pressure chemical ionization (APCI), facilitating the detection of the molecular ion (or protonated molecule) which in turn eases the derivation of possible molecular formulae. The potential of GC-(APCI)TOF-MS has recently been demonstrated in other fields, such as pesticide residue or water analysis [8–10]. To our knowledge, its application to the analysis of migrants from plastic FCMs has been rather limited. This technique has been explored for the analysis of adhesives and non-intentionally added

substances [11–13], though no work applying the APCI source was yet conducted on plastic baby bottles.

To study the migration of non-volatile compounds from FCMs, LC-MS with electrospray ionization (ESI) is the most suitable approach to be applied [14]. Only for few classes of compounds, such as pharmaceuticals or pesticides, LC mass spectral libraries are available due to the prominent spectral differences induced by the use of different ionization sources. Therefore, until now, most of the analysis of non-volatile plastic migrants has been limited to targeted approaches by monitoring pre-selected families of compounds, such as phthalates, UV-ink photoinitiators or antioxidants [14]. On the other hand, the use of HRMS is mandatory for screening purposes. LC-TOF-MS has already shown its efficiency for screening and confirmation in the analysis of forensic (illicit drugs) and environmental samples (pesticides, flame retardants, etc.) [15–20]. Furthermore, few non-targeted studies have been published on possible contaminants migrating from FCMs [21–26],

The aim of this work was to develop and apply a methodology for the identification of unknowns observed during non-targeted screening of plastic migrants from baby bottles, based on the use of low and high resolution MS. GC and LC hyphenated to a variety of mass analyzers were used for this purpose. To our knowledge, this is the first time that a combination of these techniques has been applied in a non-targeted approach to elucidate unknown migrants from plastic baby bottles. While it was not the goal of this work to give a complete overview of all detected compounds in the tested baby bottles [6], some particular examples have been selected to demonstrate the potential of the applied methodology for the elucidation of unknown plastic migrants.

Materials and methods

Materials

Samples and sample treatment

Ten polypropylene (PP) baby bottles and one polyamide (PA) baby bottle from the Belgian market [6], consisting the majority of the market share, were selected for the application of the developed methodology. The use of simulants is prescribed in the EU Regulation 10/2011 to mimic the migration testing towards real foods, leading to the selection of simulant D1 (water:EtOH (50:50)) as a simulant for milk [3]. After sterilisation of the bottles during ten minutes with boiling water, three consecutive migrations for 2h at 70°C were performed with the water-EtOH simulant. Afterwards, a non-targeted liquid-liquid extraction with ethyl acetate:n-hexane (1:1) was performed on the simulant samples as previously described [6].

The obtained organic extracts were then further concentrated to ± 75 µL under a gentle N_2 stream for analysis by GC or evaporated until dryness and dissolved in 75 µL MeOH for LC injection. All bottles were tested in duplicate. Deuterated 2,6-di-tert-butyl-4-methylphenol-D24 (Campro Scientific GmbH, Berlin, Germany) was added as an internal standard (IS) for GC analysis to the simulant prior to LLE to correct for potential variations in the extraction method or instrumental response. For LC, $^{13}C_{12}$-Bisphenol-A was selected (Cambridge Isotope Laboratories, Inc. Andover, Massachusetts, USA).

Chemicals

Methanol (gradient grade for liquid chromatography LiChrosolv) and ethyl acetate (for liquid chromatography LiChrosolv) were purchased from Merck (Darmstadt, Germany). N-hexane (for residue analysis and pesticides, 95%) was purchased from Acros Organics (Geel, Belgium). Ultrapure water was prepared by means of an Elga Purelab Prima (Tienen, Belgium). Helium (99.999%) and nitrogen (99.99%) were purchased from Air Liquide (Liège, Belgium). For GC-(Q)TOF-MS analysis hexane for ultra-trace analysis grade was purchased from Scharlab (Barcelona, Spain).For UHPLC-QTOF-MS analysis HPLC-grade methanol (MeOH), acetonitrile (ACN) and sodium hydroxide (>99%) were purchased from ScharLab (Barcelona, Spain). Formic acid (HCOOH) (>98% w/w) was obtained from Fluka. HPLC-grade water was obtained from deionized water passed through a Milli-Q water purification system (Millipore, Bedford, MA, USA). Dicyclopentyl-dimethoxysilane (>98%) was purchased from TCI chemicals (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan). Pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate) (98%) was purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany).

Methods

GC-(EI)MS

Initial non-target analyses of simulant extracts were performed with an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass selective detector (MSD) equipped with an electron impact (EI) ionization source and operated in full scan mode from *m/z* 40 to 700. The GC column was a 30 m x 0.25 mm x 0.25 µm DB-5ms column (Agilent JW Scientific, Diegem, Belgium). The temperature of the oven was set at 60°C for 3 min, and was then increased to 300°C at a rate of 10°C min^{-1} where it was held for 15 min. The total run-time was 42 min. Helium was used as a carrier gas, with a constant flow rate of 1.0 mL min^{-1}. A volume of 2 µL extract was injected so that a sufficiently detectable amount of analyte was

brought on the column. The MS spectra obtained for the migrating chemicals extracted by the simulant were compared with commercially available WILEY and NIST mass spectra libraries by use of the Agilent MSD Chemstation® for peak identification.

GC-(EI)TOF-MS

An Agilent 6890N GC system (Palo Alto, CA) equipped with an Agilent 7683 autosampler, was coupled to a GCT time-of-flight (TOF) mass spectrometer (Waters Corporation, Manchester, U.K.), operating in EI mode (70 eV). The GC separation was performed using the same column type and oven program as for the GC-(EI)MS. The interface and source temperatures were both set to 250°C and a solvent delay of 3 min was selected. The TOF-MS was operated at 1 spectrum/s acquisition rate over the mass range *m/z* 50-700, using a multichannel plate voltage of 2800 V. TOF-MS resolution was approximately 8500 at full width half maximum (FWHM) at *m/z* 614. Heptacosafluorotributylamine (Sigma Aldrich, Madrid, Spain), used for the daily mass calibration and as lock mass, was injected via syringe in the reference reservoir at 30°C to monitor the *m/z* ion 218.9856. The application manager ChromaLynx, also a module of MassLynx software, was used to investigate the presence of unknown compounds in samples. Library search was performed using the commercial NIST library.

GC-(APCI)QTOF-MS

An Agilent 7890A GC system (Palo Alto, CA, USA) coupled to a quadrupole TOF mass spectrometer XevoG2 QTOF (Waters Corporation, Manchester, UK) with an APCI source was used. The instrument was operated under MassLynx version 4.1 (Waters Corporation). Sample injections were made using an Agilent 7693 autosampler. The GC separation was performed using the same conditions as described in the previous 2 GC techniques. 1 µL was injected at 280ºC under splitless mode. Helium was used as carrier gas at 1.2 mL min^{-1}. The interface temperature was set to 310ºC using N_2 as auxiliary gas at 150 L h^{-1}, make up gas at 300 mL min^{-1} and cone gas at 16 L h^{-1}. The APCI corona pin was operated at 1.6 µA with a cone voltage of 20 V. The ionization process occurred within an enclosed ion volume, which enabled control over the protonation/charge transfer processes. Xevo QTOF-MS was operated at 2.5 spectra/s acquiring a mass range *m/z* 50–1200. TOF-MS resolution was approximately 18 000 (FWHM) at *m/z* 614. For MS^E measurements, two alternating acquisition functions were used applying different collision energies: a low-energy function (LE), selecting 4 eV, and a high-energy function (HE). In the latter case, a collision energy ramp (25-40 eV) rather

than a fixed higher collision energy was used. Heptacosafluorotributylamine (Sigma Aldrich, Madrid, Spain) was used for the daily mass calibration. Internal calibration was performed using a background ion coming from the GC-column bleed as lock mass (protonated molecule of octamethyl-cyclotetrasiloxane, *m/z* 297.0830). MassFragment software (Waters) was used to explain the fragmentation behavior of the detected compounds. This software applies a bond disconnection approach to suggest possible structures for the product ions from a given molecule.

LC-QTOF-MS

A Waters Acquity UPLC system (Waters, Milford, MA, USA) was interfaced to a hybrid quadrupole-orthogonal acceleration–TOF mass spectrometer (XEVO G2 QTOF, Waters Micromass, Manchester, UK), using an orthogonal Z-spray-ESI interface operating in positive and negative ionization modes. The UPLC separation was performed using an Acquity UPLC BEH C18 1.7 μm particle size analytical column 100 mm L × 2.1 mm I.D. (Waters) at a flow rate of 300 μL min^{-1}. The mobile phases used were A=H_2O with 0.01% HCOOH and B=MeOH with 0.01% HCOOH. The percentage of organic modifier (B) was changed linearly as follows: 0 min, 10%; 14 min, 90%; 16 min, 90%; 16.01 min, 10%; 18 min, 10%. Nitrogen (from a nitrogen generator) was used as the drying and nebulizing gas. The gas flow was set at 1000 L h^{-1}. The injection volume was 20 μL. The resolution of the TOF mass spectrometer was approximately 20,000 at full width half maximum (FWHM) at *m/z* 556. MS data were acquired over an *m/z* range of 50–1200. A capillary voltage of 0.7 and 2.5 kV was used in positive and negative ion modes, respectively. A cone voltage of 20 V was used. Collision gas was argon 99.995% (Praxair, Valencia, Spain). The interface temperature was set to 600°C and the source temperature to 130°C. The column temperature was set to 40°C.

For MS^E experiments, two acquisition functions with different collision energies were created. The first one, the low energy function (LE), selecting a collision energy of 4 eV, and the second one, the high energy (HE) function, with a collision energy ramp ranging from 25 eV to 40 eV in order to obtain a greater range of product ions. The LE and HE functions settings were for both a scan time of 0.4 s.

Calibrations were conducted from *m/z* 50 to 1200 with a 1:1 mixture of 0.05 M NaOH:5% HCOOH diluted (1:25) with acetonitrile:water (80:20). For automated accurate mass measurement, the lock-spray probe was used, using as lockmass a solution of leucine enkephalin (10 μg mL^{-1}) in acetonitrile:water (50:50) at 0.1% HCOOH pumped at 20 μL min^{-1} through the lock-spray needle. The leucine enkephalin $[M+H]^+$ ion (*m/z* 556.2771) for

positive ionization mode and $[M-H]^-$ ion (*m/z* 554.2615) for negative ionization were used for recalibrating the mass axis and to ensure a robust accurate mass measurement over time. It should be noted that all the exact masses shown in this work have a deviation of 0.55 mDa from the "true" value, as the calculation performed by the MassLynx software uses the mass of hydrogen instead of a proton when calculating $[M+H]^+$ exact mass. However, because this deviation is also applied during mass axis calibration, there is no negative impact on the mass errors presented in this article. MS data were acquired in centroid mode and were processed by the ChromaLynx XS application manager (within MassLynx v 4.1; Waters Corporation).

Data processing

GC data processing

A schematic overview of the GC approach is given in Figure 1a. The analytical strategy to perform a non-target analysis with GC-MS techniques started from the results obtained in our previous work [6]. In a first screening based on GC-(EI)MS data using commercially available WILEY and NIST libraries with Agilent MSD Chemstation® software, peaks with an area of at least 10% of the area of the internal standard were selected for identification. Only compounds with library matches above 90% were accepted as tentative candidates. When the returned match was below 90%, peaks were defined as "unidentified" as they were most probably not included in the commercial libraries and further research was conducted with GC-(EI)TOF-MS based on accurate mass data.

By means of the ChromaLynx Application Manager, a module of Masslynx software, the remaining unidentified peaks were deconvoluted and searched again in the commercial nominal mass NIST02 library. A hit list with five positive matches > 700 was generated. Next, an elemental composition calculator (maximum deviation 5 mDa) was applied to determine the five most likely formulae of the five most intense ions acquired in the accurate mass spectrum. The proposed formulae of these five fragments were then compared with the proposed molecular formulae of the top-five library hits using criteria like mass error and isotopic fit. When a possible molecular formula could be derived in this way, candidates with this particular empirical formula were searched in the Chemspider database. By using the ChromaLynx MassFragment, which is a tool for fragmentation prediction, the obtained accurate mass EI spectrum could be compared with the predicted fragments of a selected possible structure and scorings were given. In this way, a differentiation could also be made between different structures with same empirical formula and those which generate fragments which are not in accordance with the obtained experimental spectrum, could be rejected.

When no conclusive match could be obtained (e.g. more than one identity fit of possible molecular formulae with the experimental GC-(EI)TOF spectrum), the samples could be re-injected into the GC-(APCI)QTOF system to confirm or exclude preceding tentative GC-(EI)TOF identifications. Due to the reduced fragmentation generally occurring in the APCI source, a search was conducted for the accurate mass molecular ion and the protonated molecule of the suggested molecular formulae candidates from the (EI)TOF. If one of the two was present, a narrow window-extracted ion chromatogram (nw-XIC, ±0.02 Da) resulted in a chromatographic peak eluting approximately 2 minutes earlier than the values obtained in the GC-(EI)TOF-MS. If no chromatographic peak appeared performing the nw-XIC for the selected masses, the obtained spectrum at the expected retention time was manually examined for other possible ions that could be the $M^{+\bullet}$ or $[M+H]^+$. In this case, by comparing the (EI)TOF and the (APCI)QTOF spectra, generally $M^{+\bullet}$ or $[M+H]^+$ could be retrieved as often the (EI)TOF spectrum still contains minor amounts of $M^{+\bullet}$ (or $[M+H]^+$) which are more abundant in the (APCI)QTOF. Again, the elemental composition software (±5 mDa) was used to determine the molecular formula of the unknown compound. Then, the fragmentation pattern in the (APCI)QTOF of the unknown compound was studied by examining the MS^E data, which provide useful further information about the fragmentation. Normally, the HE mode offers most information about how the compound fragments as the presence of $M^{+\bullet}$ or $[M+H]^+$ diminishes and fragmentation increases. For some compounds, quite severe fragmentation occurs already in the LE mode. Experimentally recorded fragmentation patterns can also here be compared with software generated ones for possible candidates by the use of MassFragment. When commercially available, standards were bought to confirm the actual presence of the suggested compounds.

LC data processing

A graphical overview of the LC-workflow was given in Figure 1b. No commercial MS libraries of common plastic migrants are available for LC-MS, and a genuine non-target approach of the raw data would result in a far too laborious data processing. Therefore, we constructed a home-made database to facilitate a wide-scope suspect screening. By including the empirical formula of a compound in the database, the ChromaLynx software processes this against the obtained accurate mass spectra and positive matches are returned if the mass error (±0.002 Da) is appropriate. First, approximately 50 migrants that were previously detected in the alternative plastics to PC baby bottles were included in this list [5,6]. Because all analytical standards of these compounds were available to us, their experimental data

(retention time and product ions) were also included in the database. Second, the empirical formulae of around 190 common plastic additives were added, since these compounds could also migrate from the alternative plastics. Last, more than 800 compounds authorised for plastic FCMs by the European Union Regulation No. 10/2011 [3] were included in the database.

For most compounds in this database, the only criterion to obtain a positive match was to search by the exact mass of the empirical formula. This commonly led to several false positive hits. Therefore, every positive hit (a peak detected, commonly corresponding to the exact mass of the (de)protonated molecule) was checked manually evaluating the product ions and characteristic isotopic ions, leading to the tentative identification of the candidate, based on structure compatibility and comparison with available literature data. Adducts, such as $[M+Na]^+$ or $[M+K]^+$, were also included to facilitate the detection of some compounds in those cases where information existed on their possible formation. Also here, the analytical standards were purchased for confirmation when commercially available.

Results and Discussion

Selection of techniques

Until now, most analytical methods employed for the determination of plastic migrants have been focused on the targeted analysis of a restricted number of a priori selected compounds [27–29]. However, potential migrating compounds other than the target analytes cannot be detected using this approach. Electron impact (EI) ionization used in GC produces highly reproducible fragmentation spectra which makes the identification of unknown compounds possible by comparison with commercially available mass spectral libraries (e.g. Wiley, NIST). Due to its ability to obtain sensitive full scan data and accurate mass measurements [7,30,31], GC-TOF-MS and hybrid quadrupole-TOF-MS (QTOF-MS) are powerful mass analyzers for a wide variety of non-target applications for semi-volatiles [7,32]. Due to a high degree of fragmentation in EI ionization, the molecular ion has often a low abundance. This is an important limitation for structural elucidation, as the presence of the molecular ion in a mass spectrum, especially if measured at accurate mass, provides crucial information. In APCI ionization, a stable (quasi)molecular ion is formed by means of charge transfer ($M^{+\bullet}$) and/or by protonation ($[M+H]^+$). The APCI interface used in GC can be coupled with a wide range of high resolution mass analyzers (TOF, QTOF).

For LC analysis, the accurate-mass product ion spectra obtained in MS/MS mode on the QTOF-MS provide relevant structural information. However, since the pre-selection of

analyte precursor ions has to be done in the quadrupole, this results in the usual loss of isotopic pattern information. This drawback can be overcome by MS^E data-acquisition, in which both accurate-mass (de)protonated molecule (LE function) and product ions (HE function) are obtained in the same injection without the need of selecting any precursor ion. The sequential collection of LE and HE data during sample analysis is a significant advantage towards the structural elucidation of unknown compounds in a non-targeted screening approach [33].

In this manuscript, we have included a selection of examples to demonstrate the developed strategy for the elucidation of unknown migrants from plastic baby bottles. The selection of the cases was based on their ability to illustrate the contribution of each ionization technique and mass analyzer towards the final identification. A detailed overview of all identified compounds and the used techniques can be found in Table 1. Since most migrating compounds are small molecules (molecular weight < 1200 Da), the parameters to calculate the possible molecular formulae with the Elemental Composition software were generally set as follows: C: 0-50, H: 0-100, O: 0-10, N: 0-10 and P: 0-5. Other atoms were included in the search if after manual inspection of the spectrum the isotope pattern indicated the presence of other elements. A maximum deviation of 2 mDa from the measured mass was applied. When searching for the $M^{+\bullet}$ (if existing), the option 'odd-electron ions only' was added. For $[M+H]^+$, this option was 'even-electron ions only'. For fragments, both odd and even options were selected. Within the workflows proposed in Figure 1a and 1b, the criteria introduced by Schymanski et al. [34] were used towards the acceptance of an unambiguous identification of a compound. Here, five different levels of identification were defined, each with their corresponding requirements varying from a level 5 mass of interest identification to an unequivocal molecular formula (level 4), tentative candidate (level 3), probable structure (level 2) and confirmed structure (level 1). Due to the lack of commercial availability or sometimes relatively high prices of some products, not all analytical standards of tentatively identified migrants were obtained. Here, identification was only done until level 2 of these criteria.

Case study 1

In the GC-(EI)MS, an unknown chromatographic peak with a retention time of 14.30 min was detected in most PP samples tested. No firm library match was obtained and scores were very poor (<70%). Due to its detection frequency and because the intensity was comparable to that of the internal standard (± 10 µg kg^{-1} assuming an equal response factor,

which is a considerable amount for plastic migrants), this compound was of major interest. Therefore, the compound was analysed further with GC-(EI)TOF-MS (Fig 1a). When performing a database search using the accurate mass fragmentation data obtained, no improvement in the match factors was perceived. Regarding the (EI)TOF spectrum (Figure 2), the ion *m/z* 159.0843 would be assumed to be the possible $M^{+\bullet}$. A clear isotope pattern at M+1 and M+2 was seen and therefore both S and Si were included for the Elemental Composition search. This resulted in five possible molecular formulae, though only two of them ($C_6H_{13}N_3S$ and $C_5H_{13}N_3OSi$) could possibly explain the isotope pattern seen.

Looking at the LE APCI spectrum (Figure 2), *m/z* 229.1626 is the highest mass acquired, suggesting that this would be the $M^{+\bullet}$ or $[M+H]^+$ of the unknown compound and that 159.0843 is a major fragment ion. Indeed, a very small and hardly visible peak was perceived at *m/z* 228.1531 in the (EI)TOF spectrum, suggesting that *m/z* 229.1626 was $[M+H]^+$. A large number of molecular formulae (>20) were calculated, but after considering the mass errors, only three formulae remained. Of these three, already one could be discarded, as $C_5H_{21}N_6O_4$ is not an existing chemical structure. This reduced the possible empirical formulae to $C_{13}H_{24}OS$ or $C_{12}H_{24}O_2Si$. Investigating the isotope ratios and the elemental compositions of the fragments starting from these two formulae, the option implying a Si atom clearly fitted best to the obtained spectra. A number of 116 positive hits were returned when searched in the Chemspider database. At this point, a literature search using the term '$C_{12}H_{24}O_2Si$ + polypropylene' quickly returned the suggestion of dicyclopentyl-dimethoxysilane (structure 3, Figure 2). This alkyl silane is used in combination with Ziegler-Natta catalysts to increase the isotactic index of PP [35]. This structure was also suggested by Chemspider as the third most cited one. The first two structures (Figure 2) were considered as well, but already when checking the APCI spectrum with the MassFragment prediction software, the ions *m/z* 197.1363 (loss of CH_4O), 159.0844 (loss of C_5H_{10}) or 129.0736 (loss of $C_6H_{12}O$) could only be explained by structure 3. The respective masses *m/z* 215.1469, 177.0947 and 147.0844 could be explained as the adduction of a water molecule to these fragments. The inclusion of a small amount of water in the APCI source to promote the formation of the $[M+H]^+$ could explain this phenomenon as already described by Wachsmuth et al [36]. Therefore, dicyclopentyl-dimethoxysilane was retained as the probably identified migrant. The presence of this compound (level 1 identification) was afterwards unambiguously confirmed by injection of the purchased commercial standard (Figure SI-1).

Case study 2

Two peaks with an EI spectrum that exhibited similarities to those of the previously identified [6], respectively hexa- (22.54 min) and octadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester (24.22 min), were found in a PP sample at high intensities (more than 6 times the area of the IS). Library matching gave poor results (<70%) and did not suggest any structures with realistic possibilities either. The abundant presence of ion *m/z* 343.3209 in the LE function of the (APCI)QTOF suggested that for the compound related to the octadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester this had to be the $[M+H]^+$. The low abundant presence of ion *m/z* 342.3108 in the (EI)TOF spectrum indeed confirmed that ion *m/z* 343.3209 was the protonated molecule, resulting in a molecular formula of $C_{21}H_{42}O_3$. Chemspider returned 59 possible structures for this empirical formula. The presence of ions *m/z* 284.2723 and 285.2791 in the (EI)TOF and the LE (APCI)QTOF spectrum, respectively, indicated the presence of an integral stearic acid moiety ($C_{18}H_{36}O_2$) in the structure, which made us discard all other possible molecular structures and thus, only five possibilities remained (see Figure 3B). The detection of this *m/z* also revealed that, for the remaining C_3H_6O moiety, the position of the third O-atom of this molecule had to be at the ultimate or the penultimate C-atom, whether or not incorporated as an ether (structures 1 and 2) or as an alcohol group (structures 3-5) (Figure 3B). Indeed, to explain the presence of fragment *m/z* 284.2723, the rules of the McLafferty rearrangement had to be applied, stating that the sixth atom starting from the carbonyl-O has to be a hydrogen atom. In this way, structure 2 (Figure 3B) could already be rejected as a possibility. The presence of *m/z* 325.3109 in the LE (APCI)QTOF spectrum, explained by the loss of a water molecule, suggests, on the other hand, the presence of a free alcohol group instead of an ether, because the loss of water is easier and more probable in this case, which eliminates structure 1 as well. Within the available MS spectra, it was not possible though to differentiate between the remaining structural isomers of structures 3-5 to determine which the actual unknown migrant was and only a probable identification could be reached (level 2). Injection of the different analytical standards is the only way to bring a decisive answer here. For the hexadecanoic acid based unknown migrant, the same conclusions could be drawn.

Case study 3

In this case, an unknown compound with a double intensity of the IS peak was seen in the first migration step of the PA bottle, though it completely disappeared in the next migration steps. Both GC-(EI)MS and GC-(EI)TOF-MS database searches gave poor matches (<40%), indicating that the structure of the unknown migrant was very different from the

structures present in the database. The abundant ion *m/z* 394.3612 in the GC-(EI)TOF-MS (RT 31.79 min) seemed to be the $M^{+\bullet}$, which was indeed confirmed by the highly abundant presence of *m/z* 395.3638 (protonated molecule) in the LE GC-(APCI)QTOF-MS spectrum. Since no significant isotope patterns were noticed, an elemental composition search including only elements C, O, H and N resulted in a molecular formula of $C_{24}H_{46}N_2O_2$ (mass error of -0.2 mDa) for which Chemspider returned 32 hits. For this molecular formula, all fragment ions of both GC-(EI)TOF-MS and the HE of the GC-(APCI)QTOF-MS could be explained with very low mass errors (generally <2 mDa for the TOF and <0.2 mDa for the QTOF), differentiating clearly the realistic possible fragments. It was noticeable that the most abundant (EI)TOF-MS ion (*m/z* 198.1868, $C_{12}H_{24}NO$) and the second most abundant (APCI)QTOF-MS fragment ion (*m/z* 197.2014, $C_{12}H_{25}N_2$) exhibited a mass difference of only one amu with different though very similar empirical formulae, suggesting a common origin.

This observation, together with the presence in this sample of a large amount of laurolactam, a polyamide monomer with *m/z* 197.1780 and a molecular formula of $C_{12}H_{23}NO$, (GC-(EI)TOF-MS RT 17.08 min) suggested that this unknown might be a dimer of laurolactam, since its molecular formula is exactly the double of this compound and the ion *m/z* 395.3638 is two times the mass of the protonated form of laurolactam. Another evidence is the disappearance of this unknown compound after the first migration step. Because this dimer is a side-product of the polymerisation reaction, it is probably unbound in the polymer skeleton. Therefore, it can easily be transferred to the migration solution and disappear in the second migration step. Although data were rather conclusive, LC-QTOF-MS was also used to confirm the presence of this dimer, since no commercial standard was available. Indeed, the protonated monomer (*m/z* 198.1861, $C_{12}H_{23}NO$, RT: 7.41 min), the dimer (*m/z* 395.3626, $C_{24}H_{46}N_2O_2$, RT: 7.74 min) and even the trimer (*m/z* 592.5419, $C_{36}H_{70}N_3O_3$, RT: 8.39 min, most probably not eluted on GC) were seen in the LC-QTOF-MS (Figure 4B). The MS spectra of these oligomers were undeniably confirmed by Stoffers et al. [37]. Regarding the identification criteria proposed by Schymanski et al. [34], this leads us only to a level 2a identification: probable structure, unambiguous literature spectrum-structure match, but not confirmed by a reference standard. It has to be noticed though that, in this particular case, the degree of confirmation could already be considered as high, because three different ionization techniques (EI, APCI and ESI) have been applied. Yet, this is not always possible, since some compounds are not suited for both GC and LC.

Case study 4

This was based on a positive accurate mass match of a peak eluted in the LC with RT of 7.85 min having the accurate mass of bis(3,4-dimethylbenzylidene)sorbitol ($C_{24}H_{30}O_6$, Millad 3988, a nuclear clarifying agent for PP) [38], with the processed LC data in ESI+ mode. For nine out of ten PP bottles, the protonated mass of *m/z* 415.2118 was matched with an error < 2 mDa and with good isotope fittings. To confirm its presence, a literature search was conducted to compare the obtained MS spectra with available literature. McDonald et al. [38] provided characteristic MS data for this compound which indeed matched with our data (Figure 5). The protonated molecule *m/z* 415.2121 was in the LE mode also the most abundant ion. Furthermore, the $[M+Na]^+$ and $[M+K]^+$ adducts were also identified with masses *m/z* 437.1941 and 453.1682, respectively. The *m/z* 119.0862 (C_9H_{11}), which originates from the loss of one of the two dimethylbenzene moieties, was already seen in the LE function, and this ion was the most significant in the HE spectrum. Ions *m/z* 397.2010 (loss of H_2O), 295.1187 ($C_{15}H_{19}O_6$) and 277.1802 ($C_{15}H_{17}O_5$) were also retrieved in the HE function, though in relatively small abundances. The Elemental Composition calculator confirmed that all these fragments were indeed present, calculating their empirical formulas with low mass errors (<±0.8 mDa). It was noteworthy that 3,4-dimethylbenzaldehyde, a degradation product of Millad 3988, was retrieved in the GC-MS injections of all PP samples which contained this compound, confirming indirectly its presence. Therefore, we conclude the identification with a high confidence (level 2) of Millad 3988 as migrant from most PP baby bottles.

Case study 5

The accurate mass of the protonated molecule $C_{26}H_{27}N_2O_2S$, *m/z* 431.1789 (LC RT 11.9 min), corresponding to 2,5-bis(5'-*tert*-butyl-2-benzoxaolyl)thiophene, an optical brightening agent for polymers, was returned as a possible positive hit when comparing a PP sample acquired in ESI+ mode to the LC database part containing plastic additives (mass error 0.4 mDa) (Figure SI-2). Literature search [39] supported this finding, as besides the protonated molecule, it also explained the fragments *m/z* 415.1467 and 401.1303 which were seen in the HE mode and which were matched by the Elemental Composition calculator as $C_{25}H_{23}N_2O_2S$ (1 mDa error) and $C_{24}H_{21}N_2O_2S$ (2.6 mDa error), respectively. No further fragments could be seen due to the complexity of this structure. To obtain a higher confidence degree in the identification of the compound, more fragments are necessary to be obtained by applying higher collision energies.

Case study 6

The last example involves the compound Pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate), an anti-oxidant better known under its commercial name Irganox 1010. An accurate mass matching for mass *m/z* 1175.7821 ($C_{73}H_{107}O_{12}$) was obtained for this compound in all PP samples injected under ESI(-) mode in LC-QTOF-MS. Although the protonated molecule was not present in the positive mode, its deprotonated molecule was seen in the ESI- mode. Comparison of our experimental spectra with literature data only could confirm the deprotonated molecule [40]. However, the injection of an available reference standard of Irganox 1010 matched perfectly in retention time and fragmentation pattern confirming in this way the unequivocal identification of this compound (Figure SI-3).

The presence of Irganox 1010 was already suggested in our previous work because several potential degradation products of this compound were found by GC-(EI)MS analysis [6]. The compound methyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate ($C_{18}H_{28}O_3$), originating from a loss of one of the four "arms" of the original anti-oxidant (Figure SI-4), was detected in all PP samples tested before, though until now, no concrete link with its origin from Irganox 1010 could be established. This example demonstrates again the power of the simultaneous use of these complementary techniques for the analysis of unknown migrants from plastic products.

Critical considerations

An efficient analytical strategy based on the combination of several mass analyzers coupled to both gas and liquid chromatography has been applied for non-target analysis of migrating components from plastic baby bottles. The complementary use of GC-(EI)MS, GC-(EI)TOF-MS, GC-(APCI)QTOF-MS and UHPLC-QTOF-MS allowed an efficient and wide-scope target and non-target screening on samples coming from a food simulant, in this case H_2O-EtOH (50/50; v/v), that had been previously into contact with plastic baby bottles. The methodology was applied to six case studies to illustrate the analytical challenges when the mass spectra of the unknown compounds did not match with commercially available GC-(EI)MS libraries. Furthermore, the use of a home-made database including a large number of compounds of interest for detection of compounds via LC-QTOF was discussed into detail. The strategy applied in this work has been proven to be successful for the elucidation of several unknown plastic migrants, from non-polar volatile compounds to semi-polar non-volatiles. Despite the success of the (tentative) identification of some relevant compounds, the successful elucidation of unknowns is not only a matter of easily following a standardized procedure, but it also requires next to the use of several analytical techniques, experience and

creative insight of the analyst, which still makes it a challenging and quite tedious labour.

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Figure Captions:

Figure 1: Schematic overview of GC- (A) and LC (B)-methodology for the non-target screening and elucidation of unknown plastic migrants.

Figure 2: (A) (EI)TOF (top), (APCI)QTOF low energy (middle) and high energy (bottom) spectra of unknown 1 with indicated fragments originating from structure number 3. (B) Possible elemental compositions for *m/z* 159.0843 and 229.1626. (C) Top 3 Chemspider possible structures for $C_{12}H_{24}O_2Si$.

Figure 3: (A) (EI)TOF (top) and (APCI)QTOF low energy spectra of unknown 2 with structures of the most abundant fragments (B) Possible molecular structures for unknown 2 with molecular formula $C_{21}H_{42}O_3$.

Figure 4: (A) GC-(EI)TOF (top), GC-(APCI)QTOF low energy (middle) and high energy (bottom) spectra of unknown 3 with empirical formulae and fragments of the most abundant peaks. (B) LC-QTOF spectra of laurolactam monomer (top), dimer (middle), trimer (bottom). (Source structures Stoffers et al., 2003)

Figure 5: Literature ([38] +LC-MS spectrum (upper left corner) compared to the spectra obtained by us on ESI+ LC-QTOF MS (upper right LE mode, lower right HE mode) for suggested compound bis(3,4-dimethylbenzylidene)sorbitol.