



HAL
open science

Identification and quantification of migration of chemicals from plastics baby bottles used as substitutes for polycarbonate

Catherine Simoneau, Liza van den Eede, Sandro Valzacchi

► **To cite this version:**

Catherine Simoneau, Liza van den Eede, Sandro Valzacchi. Identification and quantification of migration of chemicals from plastics baby bottles used as substitutes for polycarbonate. Food Additives and Contaminants, 2012, pp.1. 10.1080/19440049.2011.644588 . hal-00777735

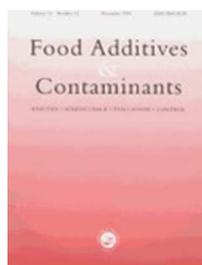
HAL Id: hal-00777735

<https://hal.science/hal-00777735>

Submitted on 18 Jan 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Identification and quantification of migration of chemicals from plastics baby bottles used as substitutes for polycarbonate

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2011-434.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	22-Nov-2011
Complete List of Authors:	Simoneau, Catherine; EC DG JRC, IHCP, EURL-FCM Van den Eede, Liza; EC DG JRC, IHCP, EURL-FCM Valzacchi, Sandro; EC DG JRC, IHCP, EURL-FCM
Methods/Techniques:	Chromatography - GC/MS, Chromatography - HPLC, Chromatography - LC/MS
Additives/Contaminants:	Baby bottles, Food contact materials, Migration, Additives general
Food Types:	
Abstract:	<p>This report presents the results of the study on the analytical identification and quantification of migration of chemicals from plastics baby bottles found in the EU market made of materials that are now present as substitutes for polycarbonate.</p> <p>449 baby bottles with a focus on 1st age or sets of bottles were purchased from 26 EU countries, Canada, Switzerland, and USA. From this collection, which contained several duplicates, a total of 277 baby bottles were analysed. The materials included different types of plastic such as polycarbonate (PC), polyamide (PA), polyethersulfone (PES), polypropylene (PP), but also silicone, and from the USA a copolyester marketed under the trade name Tritan™. The bottles were subjected to the conventional migration test for hot fill conditions i.e. 2 hours at 70°C. The simulant used was that of specified in the EU legislation 2007/19/EC for milk, i.e. 50% EtOH. In a first phase one migration was conducted since the scope of this investigation was a screening rather than a true compliance testing check. Second and third migrations were performed on selected articles when migrated substances exceeded limits specified in the legislation. In order to verify some materials, a portion of the bottle was cut to run a FT-IR fingerprint to confirm the nature of the polymer.</p> <p>The migration solutions in general showed low release of substances. Results showed that bottles made of polypropylene and silicones showed a</p>

greater number of substances in the migration solutions and in greater quantity. Chemicals from polypropylene included alkanes, which could be found in >65% of the bottles at levels up to 3500 µg/kg, and benzene derivatives in 17% of the baby bottles and found at levels up to 113 µg/kg. Some substances were found on a regular basis such as plasticisers, esters, and antioxidants (e.g. tris(2,4-di-tert-butylphenyl)phosphate, known as Irgafos 168. Some substances found were not included in the Community positive list, which means that those should not be found even in the first migration. Such substances included 2,6-diisopropyl naphthalene (DIPN), found in 4% of the bottles at levels up to 25 µg/kg, 2,4-di-tert-butyl phenol (in 90% of the bottles at levels up to 400 µg/kg.). Moreover, Bisphenol A was detected and quantified in baby bottles made of polyamide, but limited to one brand and model specific (but labelled BPA-free). Results for baby bottles made of silicone also indicated the presence of components for example potentially coming from inks (benzophenone, diisopropyl naphthalene - DIPN, which could come for example from and could be from the presence of instruction leaflets in the bottles). In the case of silicone, phthalates were also found in relevant concentrations, with levels for DiBP and DBP from the first migration test of 50-150 µg/kg. and DEHP at levels 25-50 µg/kg.

SCHOLARONE™
Manuscripts

Review Only

Identification and quantification of migration of chemicals from plastics baby bottles used as substitutes for polycarbonate

C. Simoneau, L. Van den Eede and S. Valzacchi

European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Unit Chemical Assessment and Testing, T.P. 260, Ispra Va 21027, Italy

Abstract

The results of a study on the analytical identification and quantification of migration of chemicals from plastics baby bottles found in the EU market made of materials that are now present as substitutes for polycarbonate are reported. Four hundred and forty-nine baby bottles with a focus on 1st age or sets of bottles were purchased from 26 EU countries, Canada, Switzerland, and USA. From this collection, which contained several duplicates, a total of 277 baby bottles were analysed. The materials included different types of plastic such as polycarbonate (PC), polyamide (PA), polyethersulfone (PES), polypropylene (PP), but also silicone, and from the USA a co-polyester marketed under the trade name Tritan™. The bottles were subjected to the conventional migration test for hot fill conditions i.e. 2 hours at 70°C. The simulant used was that of specified in the EU legislation 2007/19/EC for milk, i.e. 50% ethanol. In a first phase one migration was conducted since the scope of this investigation was a screening rather than a true compliance testing check. Second and third migrations were performed on selected articles when migrated substances exceeded limits specified in the legislation. In order to verify some materials, a portion of the bottle was cut to run a FT-IR fingerprint to confirm the nature of the polymer. The migration solutions in general showed low release of substances. Results showed that bottles made of polypropylene and silicones showed a greater number of substances in the migration solutions and in greater quantity. Chemicals from polypropylene included alkanes, which could be found in >65% of the bottles at levels up to 3500 µg/kg, and benzene derivatives in 17% of the baby bottles and found at levels up to 113 µg/kg. Some substances were found on a regular basis such as plasticisers, esters, and antioxidants (e.g. tris(2,4-di-tert-butylphenyl)phosphate, known as Irgafos 168. Some substances found were not included in the Community positive list, which means that those should not be found even in the first migration. Such substances included

1
2
3 2,6-di-isopropyl naphthalene (DIPN), found in 4% of the bottles at levels up to 25 µg/kg, 2,4-
4 di-tert-butyl phenol (in 90% of the bottles at levels up 400 µg/kg.). Moreover, bisphenol A
5 (BPA) was detected and quantified in baby bottles made of polyamide, but limited to one
6 brand and model specific (but labelled BPA-free). Results for baby bottles made of silicone
7 also indicated the presence of components for example potentially coming from inks
8 (benzophenone, diisopropyl naphthalene – DIPN, which could come for example from from
9 the presence of instruction leaflets in the bottles). In the case of silicone, phthalates were also
10 found in relevant concentrations, with levels for DiBP and DBP from the first migration test
11 of 50-150 µg/kg, and DEHP at levels 25-50 µg/kg.
12
13
14
15
16
17
18
19

20 **Introduction**

21
22
23 Baby bottles are widely used to feed newborns and infants. Baby bottles made of many more
24 plastics materials than in the past have appeared on the market as a direct consequence of the
25 ban of the use of Bisphenol A for the manufacture placing on the market of polycarbonate
26 infant feeding bottles (EU 2011a, EU 2011b).
27
28
29

30
31 Plastic substitutes which have massively appeared on the EU market include for
32 example polypropylene (PP), silicone, polyamide (PA), a new co-polyester under the trade
33 name 'Tritan™', and polyether sulphone (PES). Yet for these materials, chemical substances
34 such as monomers or additives may migrate from the plastic into the foodstuffs. Since infants
35 have a lower bodyweight compared to adults, their exposure to the food in contact with the
36 plastic material is higher and it is therefore particularly important to verify the absence of
37 possible causes for health concern
38
39
40
41
42
43

44
45 Although there have been many studies on release from polycarbonate baby bottles from mild
46 to harsh conditions as well as ageing (Hoekstra and Simoneau, 2011; Simoneau et al, 2011,
47 Santillana et al, 2011; Kubwabo, et al, 2009; Maia et al, 2009; Biedermann-Brem et al, 2009;
48 Biedermann-Brem et al, 2008; Cao et al, 2008; Maragou, et al, 2008; ; Ehlert et al, 2008;
49 Brede et al, 2003; Biles et al, 1997; Mountfort et al, 1997), there is a major lack of data on the
50 release of substances from the substitutes plastics now in use (Aschberger et al, 2010).
51
52
53
54

55
56 The question becomes whether these substitutes are also safe to use. The objective of this
57 study was therefore to assess the nature of materials, chemicals, and potential release of
58
59
60

1
2
3 chemicals from baby bottles found in the EU market with the aim of informing risk managers
4 on trends of evolution of the market and potential issues based on experimental data. Our
5 study focused first on developing specific methods measuring all possible components
6 migrating from the different plastics. The methods were then applied to the migration testing
7 of baby bottles from different materials and different countries of the EU.
8
9
10

11 **Materials and methods**

12 *Samples*

13
14
15
16
17 449 baby bottles or sets of bottles with a focus on first age were purchased or sent by the
18 National Reference Laboratories (NRLs) mostly in EU Member States, as well as from
19 Canada and the USA during the first half of 2010. From this collection, which contained
20 several duplicates as well as baby cups, a total of 277 baby bottles were analysed. The
21 materials of these baby bottles included different types of plastic such as Polypropylene (PP,
22 n=149), Polyamide (PA, n=28), Polycarbonate (PC, n=58), Polyethersulfone (PES, n=30), a
23 new co-polyester marketed under the trade name 'Tritan™' (n=7), silicone (n=5).
24
25
26
27
28
29
30

31 *Chemicals*

32
33 Ultrapure water was prepared from a Milli-Q purification system (Millipore); methanol,
34 acetonitrile, HPLC grade quality $\geq 99.95\%$, were purchased from Sigma Aldrich (Italy).
35 Ammonium acetate, $\geq 99.99\%$, was purchased by Aldrich (Italy). 2,2,4-Trimethyl pentane
36 (isooctane) and dichloromethane for high-performance liquid chromatography were
37 purchased by Sigma Aldrich (Italy). The following substances were used for GC-MS
38 quantification: 1,2,4-trimethyl benzene (Fluka, $\geq 99.5\%$), 1,2-dimethoxy benzene (Aldrich,
39 $>99\%$), 2,2,4-trimethyl-1,3-pentanediol-diisobutyrate (Eastman), 2,2-bis(4-hydroxyphenyl)
40 propane (Aldrich, $>99\%$), 2,4-di-tert-butylphenol (Aldrich, 99%), 2,6-di-tert-butyl-1,4-
41 benzoquinone (Aldrich, 99%), 2-butoxyethyl acetate (Aldrich, 99%), 2-ethyl-1-hexanol
42 (Fluka, $\geq 99\%$), 2-methylnaphthalene (Fluka, analytical grade), 3,4-dimethylbenzaldehyde
43 (Acros, 97%), benzophenone (Fluka, $\geq 99\%$), benzothiazole (Aldrich, 96%), bis(2-
44 ethylhexyl)phthalate (Fluka, $\geq 97\%$), 2,6-bis(1,1-dimethylethyl)-4-methylphenol (Aldrich,
45 $\geq 99\%$), 2,6-bis(1,1-dimethylethyl)-4-methylphenol -D21 (CIL Inc, 98%), dibutyl phthalate
46 (Aldrich, $\geq 99\%$), cis-9,10-epoxystearic acid (Sigma, 99%), diethyl phthalate (Sigma Aldrich,
47 99.5%), diisobutyl phthalate (Fluka, $\geq 98\%$), 2,6-diisopropyl naphthalene (Acros, 99%), n-
48 dodecane (Sigma, 99%), erucamide (Aldrich, $>97\%$), naphthalene (Fluka, $\geq 97\%$), nonanal
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 (Acros, 95%), tris(2,4-di-tert-butylphenyl)phosphite (Aldrich, 98%), methyl tridecanoate
4 (Sigma, $\geq 97\%$).
5
6
7

8 *Confirmation of the materials*

9
10 FT-IR was used to confirm the nature of the material of the baby bottles since it was not
11 always stated on the package or on the bottle. A Perkin Elmer FT-IR (Spectrum One) was
12 applied using the attenuated total reflectance mode. ATR spectra were measured with a
13 resolution of 4 cm⁻¹ in the range of 4000-650 cm⁻¹, each generated from four scans.
14
15 Identification of the polymer was achieved based on comparisons with reference spectra.
16
17

18 *Migration test*

19
20 Since most manufacturers recommended sterilisation of the baby bottle prior to use (specified
21 on the leaflet) the bottles were sterilised. The common treatment was selected as boiling in
22 water for 5 min. The bottles were then subjected to the conventional migration test for hot fill
23 conditions i.e. 2 hours at 70°C. The simulant used for milk was 50% ethanol as specified in
24 the EU legislation 2007/19/EC. This was identified as the worst case simulant for this study
25 since for juices, which would be modelled by acetic acid 3%, the age group of the infant
26 would be older than the most sensitive population of newborn where the simulant for milk
27 would apply. The simulant was pre-heated to 70°C, and a volume corresponding to the
28 specified volume of the baby bottles was added to the item. The test specimens were covered
29 with a glass plate weighted to ensure absence of evaporation and placed in a convection oven
30 for 2 hours at 70 °C. The loss of simulant was measured in preliminary tests and was shown
31 not to exceed 3%. Calibration curves were done in the 50% ethanol simulant in order to take
32 recoveries into account. After treatment the migration solution was transferred from the baby
33 bottle into a glass bottle with PTFE lined cap and left to cool down prior to analysis. An
34 aliquot was then used in glass GC vial with PTFE lined cap for analysis. A second and third
35 migration tests were performed according to the repeated use conditions for food contact
36 material (82/711/EEC as amended). The bottles were quickly rinsed with deionised water
37 between two migration tests. In a first phase only the first migration was analyzed to assess
38 the nature and amount of migrants. In cases where substances from the first migration
39 exceeded limits specified in the legislation, third migration solutions were also analysed to
40 assess the final compliance of the articles. Blank samples were also prepared from a portion
41 of the simulant used for the migration tests.
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Analysis of migration solutions

The determination and quantification of the migrants in the simulant was carried out by GC-MS. Ultra performance liquid chromatography-mass spectrometry (UPLC-MS) and HPLC with fluorescence (FLD) detection were carried out for the detection of targeted compounds such as BPA. For GC-MS a change of solvent was necessary. In this case, 10 ml of the migration solution was extracted with 1 ml isooctane prior to injection.

GC-MS analysis

The isooctane extraction solutions were analysed by GC-MS (Hewlett Packard 5890 GC) coupled with a Hewlett-Packard mass selective detector (HP 5973 MSD). The instrument was operated with a HP-5MS phase column 30 m x 0.25 mm x 0.25 μ m using Helium as a carrier gas at a flow rate of 1.3 mL/min and a splitless injection. Injection volume consisted of 1 μ L and injector block operated at 300°C. The oven programme was set at 50°C for 5 min, increased by 15°C/min to 300°C (1 min), and subsequently increased 25°C/min to 340°C and kept to this temperature to the end of the analysis. After each sequence a blank isooctane was run to clean the GC column between successive injections of samples and verify the absence of contamination or memory effect. GC-MS peak identification was performed by the Hewlett-Packard Enhanced ChemStation Software, mass spectra of the unknown compounds were matched with Wiley and NIST mass spectra libraries.

Deuterated 2,6-bis(1,1-dimethylethyl)-4-methylphenol-D21 (3.4 μ g/ml) was added to the isooctane used for the extraction of the food simulant, as internal standard, to potentially correct variations in the instrumental response. Quantification was done using different calibration curves of external standards that were prepared in 50% ethanol and subsequently extracted with isooctane to mimic the performance of the correspondent substances since not all the substances would have a 100% recovery (i.e. polar substance are poorly extracted by isooctane).

Over 70 compounds were recognised by GC-MS therefore individual quantification would be time consuming. Since the objective of this work was a screening of the potential release of different types of baby bottles, a selected number of standards were used for the quantification of either the target substance itself or substances of a similar molecular class and/or functional group.

1
2
3 Substances were quantified using the following standards: erucamide, tris(2,4-di-tert-
4 butylphenyl)phosphite (Irgafos 168), 1,2,4-trimethyl benzene, nonanal, dodecane, 2-ethyl-1-
5 hexanol, 2-butoxyethyl acetate, 3,4-dimethyl benzaldehyde, benzothiazole, 2-methyl
6 naphthalene, 1,2-dimethoxy benzene, 2,6-di-tert-butyl -1,4-benzoquinone, tridecanoic acid
7 methyl ester, 2-ethylhexanoic acid (free fatty acid).
8
9

10
11
12 In addition, alkanes, alcohols, aldehydes, and aromatic compounds. were quantified as groups.
13 For example, alkanes were calculated as sum of alkanes and were quantified on the basis of
14 the response factor of dodecane, (as they went from C7 to C20). Alcohols were calculated as
15 sum of alcohols and were quantified on the basis of the response factor of 2-ethyl-1-hexanol.
16 Aldehydes were calculated as sum of aldehydes (except for 3,4-dimethyl benzaldehyde) and
17 were quantified on the basis of the response factor of nonanal (or 3,4-dimethyl benzaldehyde).
18 Benzene derivatives were calculated as sum of benzene substances, quantified on the basis of
19 the response factor of 1,2,4-trimethyl benzene. The respective recoveries could vary with the
20 different polarities of substances (higher recovery for non-polar substances).
21
22
23
24
25
26
27
28

29 Specific substances, which were detected on a regular basis and had a relevant SML, were
30 quantified with the corresponding standard in Selected Ion Monitoring mode (SIM). These
31 substances were: 2,4-di-tert-butylphenol, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate
32 (TXIB), 2,6-diisopropyl naphthalene, benzophenone, naphthalene, butylated hydroxytoluene
33 (BHT).
34
35
36
37
38

39 For the analysis of phthalates the quantitative in SIM was used only as a screening to select
40 samples in which the level of phthalates was above an expected random ambient
41 contamination. In these cases (about 30 samples) the quantification was done in LC-MS.
42
43
44
45

46 HPLC and UPLC-MS

47 BPA was analysed from migration solutions using an HPLC (Hewlett Packard 1100) coupled
48 with Fluorescence detector. The instrument was operated with a column phenomenex Kinetex
49 C18, 150 mm x 3 mm x 2.6µm particle size, operated at a temperature of 30°C, using a flow
50 rate of 0.27 ml/min and an injection volume of 20 µl. The fluorescence detection was
51 operated with the excitation wavelength of $\lambda_{exc} = 235$ nm and an emission wavelength of
52 $\lambda_{ems} = 317$ nm. The mobile phase was composed of methanol water in proportion (68:32)
53 held for 10 minutes in isocratic conditions. The limit of detection (LOD) was 0.1 µg/kg and
54
55
56
57
58
59
60

1
2
3 limit of quantification (LOQ) was 0.3 µg/kg. The LOD was calculated based on a signal to
4 noise ratio of 3, whereas the LOQ was based on 3 times the LOD.
5
6

7
8 The migration solutions were analysed for BPA and for phthalates by UPLC-MS (Waters
9 Xevo) coupled with an electrospray interface in multiple reaction monitoring mode (MRM)
10 using a column Waters Acquity BEH C18 (100 mm x 2.1 mm x 1.7µm particle size) operated
11 at 30°C with a flow rate of 0.3 ml/min and an injection volume of 7.5 µl.
12
13

14
15
16 BPA was analysed with electrospray ionization in negative ion mode (ES-) with a mobile
17 phase of water ammonium acetate 1mM /methanol in proportion of (60:40) held for 0.3 min,
18 followed by a gradient to 20:80 in 2.7 min., and held at the ratio of 20:80 for 0.5 min. The
19 analysis was performed in multiple reaction mode (MRM) by monitoring the transition
20 reactions m/z 227→133 and m/z 227→212 with a Cone voltage of 39. The LOD was 0.1
21 µg/kg and LOQ was 0.3 µg/kg.
22
23
24
25
26

27
28 For the detection of the group of phthalates, electrospray ionization in positive ion mode
29 (ES+) was applied with a mobile phase of water ammonium acetate 1mM/methanol was
30 applied in proportion of 37:63 held for 3.5 min, followed by a gradient to 23:77 in 2.5 min
31 and subsequently another gradient to 5:95 in 1 min (held for 1.5 min). The analysis was
32 performed in multiple reaction mode (MRM) by monitoring the transition reactions m/z
33 223→149 and m/z 223→177 with a Cone voltage of 17 for diethyl phthalate, m/z 279→149
34 and m/z 279→205 with a Cone voltage of 15 for diisobutyl phthalate and dibutyl phthalate,
35 and m/z 391→149 and m/z 391→149 with a Cone voltage of 17 for diethylhexyl phthalate.
36
37
38
39
40
41
42

43 *Polymer dissolution in solvents*

44 Solvent dissolution was carried out on polypropylene baby bottles to verify the QM limits for
45 phthalates. A sub-sample of the polymer (approximately 30mg), cut from the neck of the baby
46 bottle, was added with 1 ml of xylene in a closed glass vial and heated in an oven at 135°C
47 until the complete dissolution of the polymer. The vial was then cooled down to room
48 temperature and 3ml of hexane were added to allow the precipitation of the polymer. The vial
49 was centrifuged at 2500 rpm for 5 min and an aliquot of the solvent transferred into a 2 ml
50 vial for the GC-MS analysis.
51
52
53
54
55
56

57 **Results and discussion**

1
2
3 The migration solutions in general showed low release of substances and differed not only
4 between materials but also between brands of the same material. An overview of the amount
5 of substances detected in the first migration from different types of baby bottles is given in
6 Table 1. This table lists the migrants identified by GC-MS together with the quality index of
7 recognition compared to a known spectra, and their specific migration limit (SML) when
8 specified in the legislation. The quality index gives an estimation of the confidence that can
9 be placed in the identification. Table 1 shows that all the detected compounds migrated in
10 concentrations far below their corresponding SML. Additionally, a number of unregulated
11 substances appeared in some cases in the first migration. Since these substances are not in the
12 approved list, they should not be found migrating from the material in the first migration
13 itself. The levels are however fairly low. The substances detected that were on the
14 Community list were found mostly for baby bottles made of silicone, which are not classed as
15 plastics and so this was not unexpected.
16
17
18
19
20
21
22
23
24

25
26 [Table 1 about here please]
27
28

29 ***Bottles made of polypropylene (PP)***

30
31 The largest proportion of the EU market seems to consist of bottles made of polypropylene. In
32 total, 149 bottles were investigated in this survey. These bottles tended to release a higher
33 number of substances, such as alkanes, which could be found in >65% of the bottles at levels
34 up to 3500 µg/kg, and benzene derivatives in 17% of the baby bottles and found at levels up
35 to 113 µg/kg. Some substances were found on a regular basis such as plasticisers, esters, and
36 antioxidants (e.g. tris-(2,4-di-tert-butylphenyl)phosphate, known as Irgafos 168. The migrated
37 amounts of these compounds were compliant with the limits set in the EU food contact
38 legislation. However, some substances found were not included in the EC positive list, such
39 as 2,6-di-isopropylnaphthalene (DIPN)– a compound which is more typical for ink and/or
40 recycled paper and board. This substance was found migrating in >45 % of the baby bottles at
41 levels up to 25 µg/kg. Another substance found was 2,4-di-tert-butyl phenol. This substance
42 was found fairly systematically (90%) in polypropylene baby bottles at levels up 400 µg/kg.
43 This could be a degradation product from tris-(2,4-di-tert-butylphenyl)phosphate, i.e. Irgafos
44 168. An interesting observation in some brands was the coupled migration of a group of fatty
45 acid esters: octanoic acid, 2-ethylhexyl ester, decanoic acid, 2-ethylhexyl ester, dodecanoic
46 acid, 2-ethylhexyl ester and tetradecanoic acid, 2-ethylhexyl ester. Figure 1 shows a
47 chromatogram of a GC-MS analysis of the migration solution of a polypropylene baby bottle.
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 The migrated esters were semi-quantified using 1,2,4-trimethyl benzene as an external
4 standard. The detected concentrations varied between 20 and 970 $\mu\text{g}/\text{kg}$ in the first migration
5 round. Since all four esters are represented in the EC list with the maximum migration limit of
6 60000 $\mu\text{g}/\text{kg}$ (60 mg/kg), the obtained results regarding these esters are compliant with the
7 European regulations.
8
9
10

11
12
13 [Figure 1 about here please]
14
15

16 However, polypropylene bottles also showed the presence of substances not present in the
17 Community list. In particular, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate was found in 72
18 samples out of 149 (close to 50%), in the range of 1-62 $\mu\text{g}/\text{kg}$ with an average of 5 $\mu\text{g}/\text{kg}$.
19 This substance is present in the EU plastics legislation with an SML of 5000 $\mu\text{g}/\text{kg}$, but only
20 for single-use gloves. Other substances identified and not present on the Community list
21 included 2-propenamide, 2-methyl-N-phenyl, present in 7 out of 149 polypropylene bottles at
22 levels of 90-132 $\mu\text{g}/\text{kg}$ with an average of 105 $\mu\text{g}/\text{kg}$ and N-butyl benzenesulfonamide,
23 present in 3 out 149 bottles in range of 38-108 $\mu\text{g}/\text{kg}$ with an average of 64 $\mu\text{g}/\text{kg}$.
24
25
26
27
28
29
30

31 A targeted analysis was performed for the phthalates specifically regulated in the food contact
32 legislation (diethyl phthalate DEP, disobutyl phthalate DIBP, dibutyl phthalate DBP, and
33 diethylhexyl phthalate DEHP) on bottles that had shown traces in the migration solutions. The
34 reason was that for phthalates, the EU legislation imposes a limit based on a residual content
35 know as Quantity in Material (QM) for compliance testing. The results from a dissolution re-
36 precipitation of the polymer and analysis of the extract showed the levels obtained were much
37 below the respective QMs of 0.1% mg substance per kg of material (DEP, DiBP, DEHP) and
38 0.05% mg substance per kg of material (DBP).
39
40
41
42
43
44
45

46 ***Bottles made of a copolymer marketed under the name Tritan™***

47 This material has become popular in the USA and all bottles investigated in this study were
48 purchased in the USA. It has been now authorised by Regulation EU No 10/2011 (EU 2011a)
49 as of 1 May 2011. Some baby bottles were obtained from the USA for scoping purposes in
50 foresight of the foreseen market expansion to Europe upon authorisation. The migration
51 testing from the 7 bottles tested of this material did not reveal detectable substances.
52
53
54
55
56
57
58
59
60

Bottles made of Polyamide (PA)

28 PA baby bottles were analysed, of which 27 were from one brand. The most surprising finding of the analysis of migration solutions from PA baby bottles was the identification and subsequent quantification of BPA on bottles labelled as “no Bisphenol A”. BPA was detected and quantified (both by HPLC and UPLC-MS) in 20 out of 27 bottles analysed, i.e. 77% (Table 2) in the specific brand.

[Table 2 about here please]

Six bottles released BPA in the range of 0.5-4 µg/kg, seven in the range of 15-70 µg/kg, six in the range of 100-250 µg/kg and one bottle released even more than 1000 µg/kg in the first migration. In the third migration test significant amounts of BPA could still be found in these bottles (1-330 µg/kg). These values are much higher than those found in the same survey from polycarbonate bottles (Simoneau et al, 2011).

The recognition of BPA as the migrated substance from polyamide baby bottles was confirmed by LC-MS fragmentation spectra. Daughters ions of the precursor at m/z 227 [M-H]⁻ corresponded to the ions obtained from the fragmentation of a pure standard of bisphenol A (Fig. 2). The fragmentation pathway of BPA confirmed the results in literature (Gallart-Ayala et al, 2007).

[Figure 2 about here please]

Since it was surprising to detect BPA in an article labelled as polyamide a FT-IR analysis was also performed to verify that the material was not polycarbonate (Fig. 3)

[Figure 3 about here please]

The spectra illustrated that the material was not polycarbonate. According to Commission Regulation (EU) No 10/2011 of 14 January 2011 and its amendments (EU 2011a; EU 2011b) BPA can no longer be used as an additive or as a monomer for the manufacture of polycarbonate infant feeding bottles. However when used as a monomer in materials other than polycarbonate it is still subjected to a specific migration limit of 600 µg/kg. In the context of this study it is not possible to determine whether BPA was used as an additive (not

1
2
3 allowed) or a monomer (subjected to the SML), although some studies in other context (RA,
4 2003, Brede et al, 2003) could suggest that its presence in PA would be more likely to result
5 as that of an additive and the release seen is relatively higher than the one seen for example
6 from PC when used as monomer (300 - 600 times higher).
7
8
9

10
11 In order to eliminate doubts concerning identification and quantification, a blind confirmation
12 was conducted with two independent laboratories. Samples of CH001A, CH001B, CH004,
13 CH009A, CH009B, CH009C, CH010C, CH015A, CH017, NL003A, NL008A, NL008B were
14 sent blind to both ThermoFisher Scientific and the UK Food & Environment research Agency
15 (FERA). In addition, baby bottles already tested for migration CH009A and CH015A and
16 virgin bottle CH015B were sent to FERA to conduct independent migration. The results from
17 the simulants solutions confirmed our results, with non-detectable found for samples CH010C
18 and NL008A, and concentrations within a range of 25% of those we found. The migration test
19 conducted on bottles CH009A gave a migration of 500 µg/kg, whereas the one conducted on
20 bottle CH015A gave 22 µg/kg. These results were higher than those we found in the third
21 migration (but lower than those we found in our first migration), suggested that the bottles
22 had recuperated a capacity for release in the lag time of about 4 months. The migration test of
23 the virgin bottle CH015B) gave 70 and 12 µg/kg respectively in the first and third migration.
24 These results were also close to another of our results for bottle CH016 (same brand and
25 model) giving 74 and 14 µ/kg in the first and third migration respectively (table 2). Overall,
26 the results for the PA baby bottles suggested not only a seemingly abnormal presence of BPA
27 for this type of polymer but also an illicit one as the bottles were labelled 'NO Bisphenol-A'.
28 Table 2 shows that baby bottles containing BPA were of the same brand, but in particular 2
29 models mostly available in Switzerland and the Netherlands, with larger migration seen on the
30 smaller volume (125ml) bottles.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45

46 It should also be noted that other substances migrated from the investigated bottles made from
47 this type of polyamide. In particular, cyclododecene which is not included in the EC positive
48 list, was found in nearly all (85%) of the bottles investigated, in concentrations from 10-60
49 µg/kg. It should be noted that this substance was not found in other materials. Studies
50 indicate that cyclododecene can be an intermediate for the synthesis of monomers used in the
51 manufacture of polyamide, co-polyamides and polyesters (Adams et al, 2007). DIPN (and
52 naphthalene) were also found in respectively 6 out of 28 bottles (21%) for DIPN and 7 out 28
53 bottles for naphthalene, but in very low levels 1-2 µg/kg. Again for these substances more
54
55
56
57
58
59
60

1
2
3 common to paper and board, the cause could be from the presence of leaflets inside the bottles
4 since benzophenone was also present in some of the bottles under consideration.
5
6

7 8 ***Bottles made of Silicones***

9
10 Although silicone articles are not regarded as "plastic materials and articles" as laid down by
11 the EU Framework Regulation 1935/2004 of plastic materials in contact with foodstuffs,
12 preliminary results were obtained from 5 samples purchased and analysed since this material
13 can be found in the EU market. This material generally showed migration of a greater number
14 and extent substances than polypropylene, as shown as Figure 3.
15
16

17
18
19 [Figure 3 about here please]
20
21

22
23 The most striking finding was the presence of phthalates in the migration solutions, more
24 specifically diisobutyl phthalate (DiBP), dibutyl phthalate (DBP) and diethylhexylphthalate
25 (DEHP). The levels for DiBP and DBP from the first migration test were in the range 50-150
26 $\mu\text{g}/\text{kg}$. DEHP was found to a lesser extent at levels 25-50 $\mu\text{g}/\text{kg}$.
27
28

29
30 All bottles also released what could be considered ink or cardboard related substances such as
31 DIPN, benzophenone, and naphthalene. DIPN in particular (not regulated for plastics) could
32 be found in all the baby bottles analysed, at levels of 5-20 $\mu\text{g}/\text{kg}$. Finally all the bottles also
33 released a significant number of aldehydes (not found in any of the other bottles investigated
34 with an exception of a few bottles made from polypropylene), to level up to 700 $\mu\text{g}/\text{kg}$ in the
35 first migration which remained to 60 $\mu\text{g}/\text{kg}$ at the third migration.
36
37

38
39 Due to the ban of polycarbonate bottles it may be expected that more silicone bottles could be
40 one of the choices for baby bottles on the European market. There is therefore a need to
41 further investigate this material, especially in view of the suspected endocrine disrupting
42 characteristics of phthalates.
43
44

45 46 47 ***Bottles made of Polyethersulphone (PES)***

48
49 The migration solutions of 30 polyethersulphone bottles were analysed to determine the
50 presence of other migrants. Generally, migration solutions showed a very low release (less
51 than 150 $\mu\text{g}/\text{kg}$) of mostly one or two compounds but the majority of the analysis indicated no
52 migration at all. However, one brand released more compounds than the average
53
54
55
56
57
58
59
60

1
2
3 polyethersulfone article. From these articles a noticeable amount of benzophenone migrated.
4 Since these concentrations were higher than the SML (600 µg/kg) a second and third
5 migration test were performed. Analysis of the third migration indicated the level of
6 benzophenone had decreased within regulatory limits. Remarkably, these articles contained a
7 piece of cardboard when purchased. This implies the benzophenone could have migrated from
8 the polymer as well as from the cardboard. The bottle was dissolved with DCM and re-
9 precipitated with methanol but the resulting extract showed only trace amounts of
10 benzophenone, which seems to confirm the hypothesis of a contamination by the board.
11 Furthermore, the migration from these typical polyethersulfone bottles seemed to indicate the
12 presence of a substance identified as close to decahydro-4,4,8,9,10-pentamethylnaphthalene at
13 levels between 12 and 42 µg/kg in the simulant after the third migration. As the quality index
14 was below 60, the confirmation of identity of the substance needs further investigations since
15 as such, it is not listed in the EC positive list.
16
17
18
19
20
21
22
23
24
25

26 In a previous study (Simoneau et al, 2011) migration of diphenyl sulphone, 4,4'-
27 dihydroxydiphenyl sulphone (Bisphenol S) and 4,4'-dichlorodiphenyl sulphone was
28 specifically measured by UPLCS-MS and HPLCPLHP. The data obtained showed that the
29 migration of all 30 bottles remained much below their migration limits of 3000 µg/kg for
30 diphenyl sulphone and 50 µg/kg for Bisphenol S and 4,4'-dichlorodiphenyl sulphone after the
31 first migration test. According to our results, all the analyzed baby bottles made of PES were
32 therefore compliant with the European regulations concerning the migration of Bisphenol S,
33 diphenyl sulphone and 4,4'-dichlorodiphenyl sulphone.
34
35
36
37
38
39
40
41

42 ***Bottles made of Polycarbonate (PC)***

43 In total, 58 baby bottles of Polycarbonate were investigated to verify the presence of BPA and
44 other migrated compounds. The results of the release of BPA from polycarbonate bottles are
45 presented in a previous study (Simoneau et al, 2011). Another 18 bottles were also analysed
46 by GC-MS to investigate migration of other compounds. These results did not show any
47 noticeable release of compounds from polycarbonate baby bottles.
48
49
50
51

52 **Conclusion**

53 Overall, the findings with respect to the different materials led to the following conclusions:
54 No issue was found for bottles made of polyethersulphone nor for the polymer Tritan™ in
55 view of release of chemical substances. For the latter, the survey sample size was limited and
56
57
58
59
60

1
2
3 may need further monitoring once reaching the EU market. A significant issue for polyamide
4 bottles was identified as the migration of BPA in relevant amounts. Bottles made from
5 polypropylene showed substances which are not on the positive list, and in particular DIPN
6 present in about 45 % of the 149 bottles; a significant issue might arise from the presence of
7 silicone baby bottles on the EU market due to the migration of phthalates
8
9
10

11 12 13 **Acknowledgment:**

14 The authors wish to thank the European Union National Reference Laboratories for
15 contributing to sending relevant samples. We also thank O. Scheibner from Thermo Fischer
16 Scientific (Bremen) for the confirmation of the identification of BPA from migration
17 solutions. Finally we wish to thank E. Bradley and M. Driffield for their work in blind
18 confirmation of both migrations solutions and migrations tests to confirm the BPA presence
19 and levels from PA bottles.
20
21
22
23
24
25
26
27

28 **References:**

29
30
31 Adams,R.D., Boswell, E.M, Captain, B., Hungria, A.B., Midgley, P.A., Raja, R., Thomas,
32 J.M. (2007) Bimetallic Ru–Sn Nanoparticle Catalysts for the Solvent-Free Selective
33 Hydrogenation of 1,5,9-Cyclododecatriene to Cyclododecene, *Angew. Chem. Int. Ed.* 46:
34 8182 –8185
35
36
37
38

39 Aschberger K., Castello P., Hoekstra E., Karakitsios S., Munn S., Pakalin S., Sarigiannis D.
40 2010. Bisphenol A and baby bottles: challenges and perspectives; Publication Office of the
41 European Union, Luxembourg, JRC Scientific and Technical Report, EUR 24389 EN
42
43
44

45
46 Biedermann-Brem, S., Grob, K. 2009. Release of bisphenol A from polycarbonate baby
47 bottles: Water hardness as the most relevant factor, *European Food Research and Technology*,
48 228:679-684.
49
50

51
52 Biedermann-Brem, S., Grob, K., Fjeldal, P. 2008. Release of bisphenol A from polycarbonate
53 baby bottles: Mechanisms of formation and investigation of worst case scenarios. *European*
54 *Food Research and Technology*, 227:1053-1060.
55
56
57
58
59
60

1
2
3 Biles, J.E., McNeal, T.P., Begley, T.H., Hollifield, H.C. 1997. Determination of Bisphenol-A
4 in Reusable Polycarbonate Food-Contact Plastics and Migration to Food-Simulating Liquids.
5 Journal of Agricultural and Food Chemistry, 45:3541-3544.
6
7

8
9 Brede, C., Fjeldal, P., Skjevraak, I., Herikstad, H. 2003. Increased migration levels of
10 bisphenol A from polycarbonate baby bottles after dishwashing, boiling and brushing. Food
11 Additives and Contaminants, 20: 684-689.
12
13

14
15
16 Cao, X.-L., Corriveau, J. 2008. Migration of bisphenol A from polycarbonate baby and water
17 bottles into water under severe conditions Journal of Agricultural and Food Chemistry, 56:
18 6378-6381.
19
20

21
22
23 ECB 2003. Bisphenol A: European Union Risk Assessment Report (CAS No. 80-05-7), Vol
24 37. EINECS No. 201-245-8. Luxembourg:European Chemicals Bureau
25
26

27
28
29 EEC, 1982, Council Directive 82/711/EEC of 18 October 1982 laying down the basic rules
30 necessary for testing migration of the constituents of plastic materials and articles intended to
31 come into contact with foodstuffs *OJ L 297, 23.10.1982, p. 26-30*
32
33

34
35 EC, 2007, Commission Directive 2007/19/EC of 30 March 2007 amending Directive
36 2002/72/EC relating to plastic materials and articles intended to come into contact with food
37 and Council Directive 85/572/EEC laying down the list of simulants to be used for testing
38 migration of constituents of plastic materials and articles intended to come into contact with
39 foodstuffs. *OJ L 91, 31.3.2007, p. 17-36*
40
41
42

43
44 EU 2011a, Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials
45 and articles intended to come into contact with food, *OJ L 12, 15.1.2011, p. 1-89*
46
47
48

49
50
51 EU 2011b, Commission Implementing Regulation (EU) No 321/2011 of 1 April 2011
52 amending Regulation (EU) No 10/2011 as regards the restriction of use of Bisphenol A in
53 plastic infant feeding bottles *OJ L 87, 2.4.2011, p. 1-2*
54
55
56
57
58
59
60

1
2
3 Ehlert, K.A., Beumer, C.W.E., Groot, M.C.E. 2008. Migration of bisphenol A into water from
4 polycarbonate baby bottles during microwave heating. *Food Additives and Contaminants -*
5 *Part A* 25:904-910.
6
7

8
9
10 Gallart-Ayala, H., Moyano, E., Galceran, M.T. 2007. Liquid chromatography/multi-stage
11 mass spectrometry of bisphenol A and its halogenated derivatives. *Rapid Commun. Mass*
12 *Spectrom.*, 21:4039–4048.
13
14

15
16 Hoekstra, E. and Simoneau, C. 2011. Release of bisphenol A from polycarbonate: a review,
17 *Critical Reviews in Food Science and Nutrition* (In Press).
18
19

20
21 Kubwabo, C., Kosarac, I., Stewart, B., Gauthier, B.R., Lalonde, K., Lalonde, P.J. 2009.
22 Migration of bisphenol A from plastic baby bottles, baby bottle liners and reusable
23 polycarbonate drinking bottles. *Food Additives and Contaminants - Part A* 26: 928-937.
24
25

26
27
28 Maia, J., Cruz, J.M., Sendón, R., Bustos, J., Sanchez, J.J., Paseiro, P. 2009. Effect of
29 detergents in the release of bisphenol A from polycarbonate baby bottles. *Food Research*
30 *International*, 42:1410-1414.
31
32

33
34 Maragou, N.C., Makri, A.A., Lampi, E., Thomaidis, N.S., Koupparis, M.A. 2008. Migration
35 of bisphenol A from polycarbonate baby bottles under real use conditions. *Food Additives*
36 *and Contaminants - Part A* 25:373-383.
37
38

39
40
41 Mountfort, K.A., Kelly, J., Jickells, S.M., Castle, L. 1997. Investigations into the potential
42 degradation of polycarbonate baby bottles during sterilization with consequent release of
43 bisphenol A. *Food Additives and Contaminants*, 14:737-740.
44
45

46
47
48 Santillana, M.I, Ruiz, E., Nieto, M.T, Bustos, J., Maia, J., Sendón, R., and Sánchez, J.J. 2011.
49 Study on the migration of bisphenol a from polycarbonate baby bottles purchased in the
50 Spanish market by liquid chromatography and fluorescence detection, *Food Additives and*
51 *Contaminants*, 28: 1610-1618
52
53
54
55
56
57
58
59
60

1
2
3 Simoneau, C., Valzacchi, S., Morkunas V., Van den Eede, L. 2011. Comparison of migration
4 from polyethersulphone and polycarbonate baby bottles, Food Additives and Contaminants
5 (In Press)
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Peer Review Only

Table 1: Migrants from different type of baby bottles detected by GC-MS (with index of recognition >80%)

Migrant	CAS	Quality	SML (mg/kg)	Polypropylene (n=149)			Polyamide (n=28)			Silicone (n=5)		
				n	range (µg/kg)	average (µg/kg)	n	range (µg/kg)	average (µg/kg)	n	range (µg/kg)	average (µg/kg)
2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB)	6846-50-0	100	5 ¹	72	1-62	5	3	2	2	5	14-574	159
2,2-bis(4-hydroxyphenyl)propane (BPA)	80-05-7	100	0.6 ²				17 ³	1-1005	106			
2,4,6-trimethyl benzaldehyde	487-68-3	90	n/a							1	94	
2,4-dimethyl benzaldehyde	15764-16-6	87	60	6	21-62	47				1	94	
2,4-di-tert-butyl phenol	96-76-4	100	60	133	1-419	49	1	3		4	26-221	103
2,6-diisopropyl naphthalene (DIPN)	24157-81-1; 38640-62-9	100	n/a	69	1-23	5	6	1-2	1	5	4-23	12
2,6-di-tert-butyl-p-benzoquinone	719-22-2	97	60							2	341-382	361
2-butoxyethyl acetate	112-07-2	86	60	6	139-778	354						
2-methylnaphthalene	91-57-6	80	60	1	3		1	3				
2-propenamide, 2-methyl-N-phenyl	1611-83-2	86	n/a	7	90-132	105						
2-propenoic acid, 3-(4-methoxyphenyl)-2-ethylhexyl ester	5466-77-3	95	n/a							1	175	
2-propenoic acid-2-ethylhexyl ester	103-11-7	86	0,05							3	24-72	76
3,5,5-trimethyl-2-cyclohexen-1-one	78-59-1	91	60							1	88	
4-ethylbenzaldehyde	4748-78-1	91	60							1	92	
4-tert-butylcyclohexyl acetate	32210-23-4	90	n/a							1	145	
9-octadecenamide (oleamide)	301-02-0	93	60	2	227-2487	1357						
9-octadecenoic acid, methyl ester	112-62-9	99	60	12	18-294	65						
acetic acid, 2-ethylhexyl ester	103-09-3	86	60							4	23-76	51
alpha-methylstyrene	98-83-9	86	0.05									
benzaldehyde-4-methylthio	3446-89-7	90	n/a							1	33	
benzoic acid, 4-ethoxy-ethyl ester	23676-09-7	91	3,6							1	23	
benzophenone	119-61-9	100	0.6	39	1-286	43	2	2	2	5	11-637	184
butylated hydroxytoluene (BHT)	128-37-0	100	3	14	1-156	44				3	1-3	2
camphor	76-22-2	96	60 ⁴							3	18-147	87
cyclododecene	1501-82-2	97	n/a				17	6-63	29			
cyclohexanone	108-94-1	93	60							1	109	

Migrant	CAS	Quality	SML (mg/kg)	Polypropylene (n=149)			Polyamide (n=28)			Silicone (n=5)		
				n	range (µg/kg)	average (µg/kg)	n	range (µg/kg)	average (µg/kg)	n	range (µg/kg)	average (µg/kg)
cyclohexanone-5-methyl-2-(1-methylethyl)	10458-14-7		60						2	20-128	74	
decanoic acid 2-ethylhexyl ester	73947-30-5	86	60	8	28-170	113						
dodecanoic acid 1-methylethyl ester	10233-13-3	83	60	16	29-3131	570			3	356-1464	739	
dodecanoic acid 2-ethylhexyl ester	20292-08-4	86	60	9	15-1220	692						
dodecanoic acid, methyl ester	111-82-0	91	60						1	45		
erucamide	112-84-5	100	60	9	138-791	303			2	73-160	116	
eucalyptol	470-82-6	91	60	2	237-391	314			2	149-589	369	
hexadecanoic acid	57-10-3	99	60	7	1590-2965	2347			1	9540		
hexadecanoic acid methyl ester	112-39-0	97	60	7	19-98	49						
hexadecanoic acid,2-hydroxy-1-(hydroxymethyl) ethyl ester	23470-00-0	91	60	8	21-208	49						
methyl 3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	6386-38-5		60	38	15-34	23			3	29-52	37	
naphthalene	91-20-3	100	60	27	1-11	2	7	1-5	2	4	2-4	3
N-butyl benzenesulfonamide	3622-84-2	94	n/a	3	38-108	64						
octadecanoic acid	57-11-4	99	60	5	792-10416	3449			1	2256		
octadecanoic acid, ethyl ester	111-61-5	97	60	8	17-47	25						
octanoic acid,2-ethylhexyl ester	63321-70-0	90	60	8	38-235	138						
tetradecanoic acid 2-ethylhexyl ester	29806-75-5		60	4	42-59	53						
tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168)	31570-04-4	100	60	132	4-1884	144			1	36		
benzenes				26	1-113	26						
alcohols				5	72-1039	459			4	303-1563	668	
aldehydes				9	16-140	54			5	34-676	123	
alcanes				99	4-3414	187			2	37-41	39	

1: To be used in single-use gloves only; 2: Not to be used for the manufacture of polycarbonate infant(*) feeding bottles(**); with: (*) Infant as defined in Article 2 of Directive 2006/141/EC and (**) This restriction is applicable from 1 May 2011 as regards the manufacture and from 1 June 2011 as regards the placing on the market and importation into the Union. SML applicable for the use as monomer only; 3: Total of 28 polyamide baby bottles were analysed by HLPC to verify the presence of BPA; 4: Warning: there is a risk that the migration of the substance deteriorates the organoleptic characteristics of the food in contact; *: in this case the standard used was that of the substance itself, making the identification 100%.
n/a: not applicable: "substances not included in the European legislation)"

Table 2: identification of BPA in polyamide using HPLC and UPLC-MS.

product name	labelling	volume	sample	ppb (UPLC) 1st migration	ppb (HPLC) 1st migration	ppb (HPLC) 3rd migration
Brand A	no bisphenol A	125	AT003	nd	nd	nd
Brand B model 1	no bisphenol A	250	NL009	nd	nd	nd
	no bisphenol A	150	CH010 A	nd	nd	nd
	no bisphenol A	150	CH010 B	nd	nd	nd
	no bisphenol A	150	CH010 C	nd	nd	nd
Brand B model 2	no bisphenol A	150	BE009	nd	nd	nd
Brand B model 3	no bisphenol A	250	CH017	nd	3	nd
Brand B model 4	no bisphenol A	250	CH004	7	3	nd
	no bisphenol A	250	CH013 A	nd	nd	nd
	no bisphenol A	125	CH014	29	29	6
	no bisphenol A	125	CH015A	36	30	7
	no bisphenol A	125	CH016	83	74	14
Brand B model 5	no bisphenol A	250	CH011 A	nd	1	nd
	no bisphenol A	250	CH011 B	nd	1	na
	no bisphenol A	250	CH011 C	nd	1	na
	no bisphenol A	250	NL003 A	31	26	nd
	no bisphenol A	250	NL003 B	2	1	nd
	no bisphenol A	250	NL008 A	5	nd	nd
	no bisphenol A	250	NL008 B	36	29	6
	no bisphenol A	250	NL011 A	2	4	1
	no bisphenol A	125	NL012 A	128	119	27
	no bisphenol A	125	CH001 A	103	111	16
	no bisphenol A	125	CH001 B	129	129	29
	no bisphenol A	125	CH001 C	23	17	4
	no bisphenol A	125	CH009 A	1000	1005	329
	no bisphenol A	125	CH009 B	268	262	127
no bisphenol A	125	CH009 C	164	147	83	
no bisphenol A	125	CH018	167	136	31	

Note: nd: non detectable; na: not analysed

Figure 1: GC-MS chromatogram of LT007, a polypropylene baby bottle

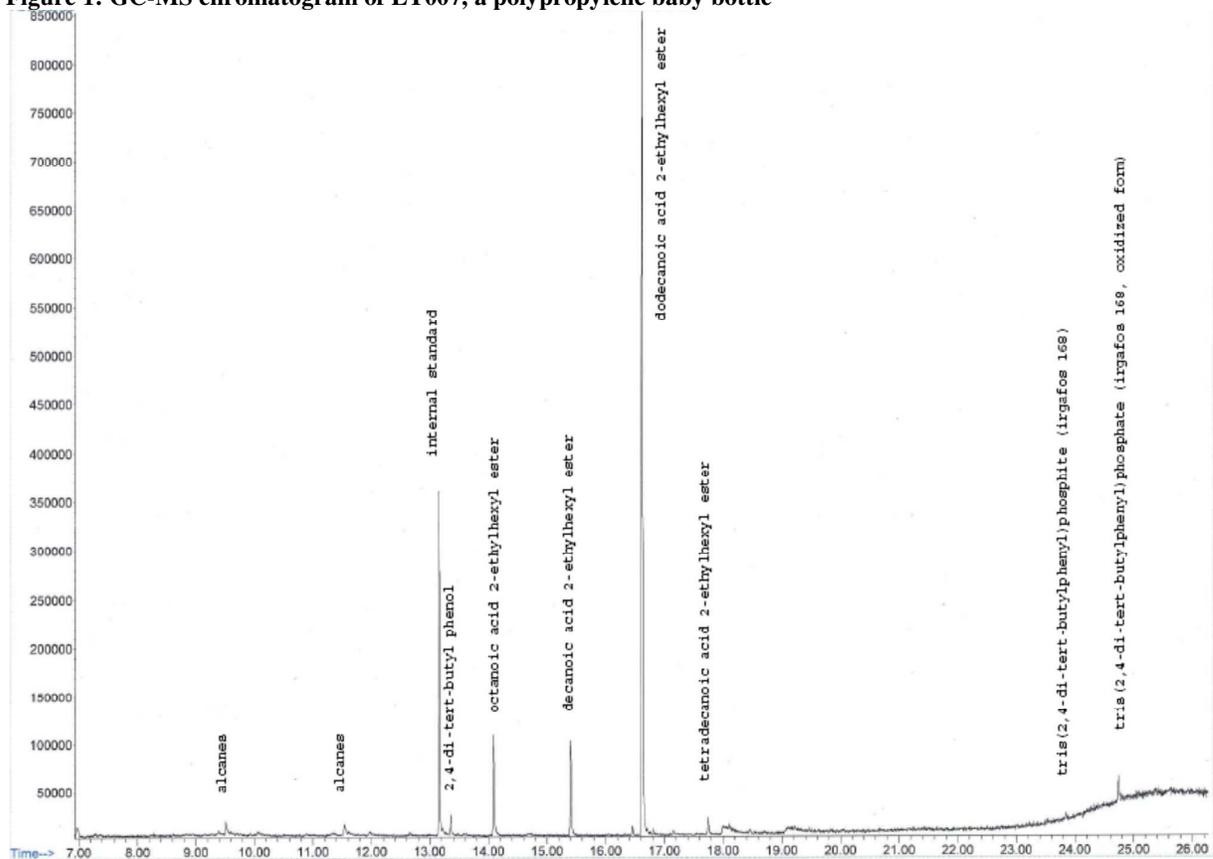


Figure 2: MS-MS spectra of BPA from baby bottle CH009A-PA (upper spectrum) and BPA standard (lower spectrum)

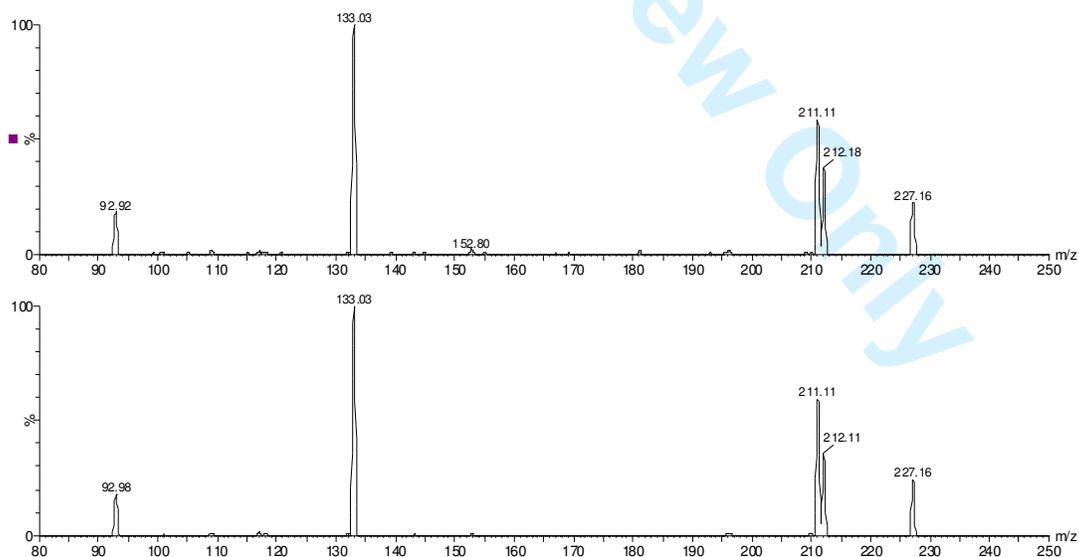


Figure 3: FT-IR spectrum of a polyamide baby bottle (CH009A-PA) and a polycarbonate baby bottle (FIN003-PC)

