Screening of diesters of ortho phthalic acid in printed baby bibs in the European market

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Abstract

A screening exercise targeting ortho-phthalates in twenty two plastic baby bibs collected in European market was performed. A GC-MS method was used with a limit of detection ranging from 0.1 to 0.6 $mgkg^{-1}$ bib. The most frequently detected phthalates were di-n-butyl phthalate and di-iso-butyl phthalate, in nearly all samples. The latter was detected often in higher concentration than the first one, suggesting its intended use. Overall, the highest levels were detected for benzyl butyl phthalate, with 6 samples presenting concentration from 13 - 47 $mgkg^{-1}$ and one sample with the highest value of 65 $mgkg^{-1}$. Results indicate that several non-authorised phthalates are being used either in the plastic or in the printing inks. Worst case migration calculations indicate that DEP, DAP and DIBP exceed the 0.01 $mgkg^{-1}$, and therefore, determination of experimental migration is needed to conclude on compliance of baby bibs with the European and Swiss legislation. Bibs are considered, accordingly to European legislation, as FCMs and therefore, they should comply with the applicable rules, restrictions and limits. These articles should be included in surveillance plans, focusing in monitoring bibs composition, migration and the application by industry of good manufacturing practices.

Keywords: phthalates, plastic baby bibs, potential migration, plasticisers

Introduction

Diesters of ortho-phthalic acid (dialkyl or alkyl esters of 1,2-benzenedicarboxylic acid), commonly referred to as phthalates, are amongst the most common organic contaminants in both the environment and consumer products. Phthalates are not chemically bound to polymer chains and therefore they may migrate into food at rates and levels, which like for other migrants, depend on the contacting conditions (Poças, 2018).

Exposure to phthalates is well known to have adverse effects on the health and development of humans, especially for children. Humans can be exposed to these phthalates through various routes, the most concerning being ingestion (EFSA, 2019). Infants and young children, due to their hand-to-mouth behaviour when handling different articles, are potentially more exposed than adults. Furthermore, these groups of population have specific physiological and developmental characteristics, as well as nutritional needs and food consumer patterns different than adults. These differences justify a particular attention in risk assessment of chemicals they are exposed to. This has impact on the rules and criteria applicable to foods and specific materials and articles intended for children consumption, use and handling.

Phthlates are used as plasticizers in many plastics applications including packaging and other food-contact materials (FCM), such as tubing and equipment parts used in food processing, handling and storage (Pereira et al. 2019) and are also used in non-plastic articles, such as printing inks, coatings and adhesives. Higher molecular weight phthalates, such as di-2-ethylhexyl phthalate (DEHP), are primarily used as plasticizers to soften polyvinyl chloride (PVC) products, while the lower molecular weight phthalates, such as diethyl phthalate (DEP), di-n-butyl phthalate (DBP), and butyl benzyl phthalate (BBP), are widely used as solvents and technical support agents or production aids such as for example pasting agent for catalysts (Cao et al., 2010). There is a trend for replacing ortho phthalates by other plasticizers families, such as terephthalates, benzoates, citrates, trimellitates, carboxyl adipates, phosphates and polymeric plasticizers.

Several phthalates are authorised for use in plastic FCM under the European harmonised legislation (EU, 2011). From those, DEHP, DBP and BBP are identified as substances of very high concern (SVHC) under the REACH Regulation due to their toxicity for reproduction and endocrine disrupting properties for human health. DEHP is additionally considered to be endocrine disruptor for the environment (EFSA, 2019). The Commission Regulation (EU) 2018/2005 (updates the REACH - Regulation (EC) No 1907/2006) restricts the level of the phthalates DEHP, BBP, DBP and di-iso-butyl phthalate (DIBP) in any plasticized material in articles used by consumers or in indoor areas, including toys and childcare products, after June 2020. However, this restriction does not apply to food contact materials that are regulated by Regulation (EU) No 10/2011. It is worthy to note that the Regulation (EU) 2018/2005 also updated the definition of "childcare" to the following: "childcare article' shall mean any product intended to facilitate sleep, relaxation, hygiene, the feeding of children or sucking on the part of children". Plastic baby bibs are used for assisting on feeding infants and toddlers, so stakeholders may wrongly assume that bibs should comply with the REACH regulation only and ignore the need for complying with the food contact rules, which is more restrictive. While the REACH regulation defines limits for the concentration of phthalates in the plasticised material in articles (individually or in any combination, no greater than 0.1 % (m/m)), the FCM legislation sets lower concentration limits, but additionally sets restrictions regarding the type of article and migration limits.

According European framework legislation, baby bibs are considered a food contact material (FCM) as they can reasonably be expected to be brought into contact with food or to transfer their constituents to food under normal or foreseeable conditions of use (European Union Regulation nº 1935/2004). During its use, the baby spilt food and saliva on the bib, which is then typically fed again into the baby mouth, by the care-taker (Galbiati et al., 2020). Additionally, babies can chew and suck the bib. This product has not been targeted in surveys regarding phthalates in food contact materials. The objective of this work was to screen plastic baby bibs, collected in the European market, for ortho phthalates, to determine the potential of migration and to pinpoint the need for addressing these articles in surveillance plans.

Material and methods

Samples

Twenty-two bibs were purchased from all around Europe: 4 in Italy, 5 in Spain, 5 in Portugal, 3 in Ireland, 2 in Slovenia, 2 in Germany and 1 from Denmark. All samples were purchased directly in specialized or non-specialized stores and none was acquired by e-commerce channel. In order to prevent any cross contamination, samples were manipulated and stored wrapped in aluminum foil during the transport to the laboratory in Portugal. The material of the bibs was confirmed by (DSC) Dynamic Scanning Calorimetry (Shimadzu Corporation), through the determination of thermal transitions. Most of the bibs were made of polyethylene/vinyl acetate (PEVA) and a few of them were in polyamide (PA) and PE. The material grammage was in average 1.5 gdm^{-2}.

Phthalates analysed

The phthalates analysed are described in Table 1. From these DBP, BBP, DEHP, DINP and DIDP are authorized under the Regulation nº 10/2011 applicable to plastics in contact with food, with the following respective specific migration limits (SMLs): 0.3, 30, 1.5 and 9 mgkg-1 for the sum of both DINP and DIDP. DAP is authorized with a migration level that should be non-detectable, which in practice is assumed as 0.01 mgkg-1 as for the non-authorized phthalates. The standards were supplied by Fluka® (DMP, DEP, DIBP, DNOP, DIDP), Sigma Aldrich® (DAP, DBP, DEHP, DCHP), Chem Service® (DHP), Jayflex® (BBP, DINP) and AccuStandard® (DIAP). The identification of the detected phthalates was performed by matching spectra with library NIST MS Search (Version 2.2, 2014), following confirmation with standards.

Background contamination management

To minimise the analytical background levels of those phthalates that are ubiquitous, the following measures were taken:

- All the material used to handle the samples were cleaned between samples to avoid cross contamination;

- Glassware rinsed with hexane and acetone; then heated at 160 °C (overnight) prior to use;

- Disposable glass centrifuge test tubes used for extraction and concentration steps;

- Chromatographic analyses undertaken in a different laboratory from the one used for preparation of analytical standards and handling the samples;

- Residual contamination in blank injections subtracted from samples;

- Solvent injection after calibration curve analysis and between every samples;

- Triple super clean gas filter installed into gas supply of gas chromatograph.

Qualitative analysis of phthalates

Ca 1 g of each sample was cut (3x3 mm), weighted and extracted with 10 ml dichloromethane (DCM) with the internal standard (Benzophenone d10) at 0.05 mgkg-1. Extraction conditions were: 40 °C for 24 hours with occasional stirring, followed by ultrasonic bath for 30 min, centrifugation (2500 rpm for 7 min) and filtration (0,45 µm PTFE membrane) before chromatography analysis. A blank of DCM was also prepared.

Quantitative analysis of phthalates

Calibration curves, using deuterated phthalates (Sigma-Aldrich®) as internal standards, were prepared according to the regulatory status of the specific phthalate, in the range of 0-0.4 mgL-1 for all phthalates, except for DIDP and DINP that the range of 0-2 mgL-1 was applied. DBP-d4 (CAS n° 93952-11-5) was used as internal standard for DMP, DEP, DAP, DIBP and DBP, DEHP-d4 (CAS n° 93951-87-2) was used for DHP, BBP and DEHP, and DNOP-d4 (CAS n° 93952-13-7) for DNOP, DINP, DIDP. The calibration solutions were prepared in the extraction solvent (DCM).

Ca 1 g of each sample in replicate was cut, weighted and extracted with 10 ml dichloromethane (DCM) with the internal standard solution of deuterated phthalates at

0.25 mgL-1. The same extraction conditions as for qualitative analyses were applied following chromatography analysis. A blank of DCM was also prepared.

Analysis by gas chromatography GC-MS

The analyses were performed in a system Bruker® Scion 456 TQ GC/MS, with the following operation conditions in the qualitative analyses: vector gas Helium at 1 ml/min; injection temperature 320 °C; column Supelco® SLB-5ms (30m x 0,25 mm I.D. Df= 0,25 µm); oven temperature 40 °C for 5 min, rate of 10 °C/min up to 320 °C and 320 °C for 25 min; volume of injection of 1 µl, splitless time 0,5 min. In the quantitative analyses slightly different conditions were applied: oven temperature 80 °C for 1 min, rate of 10 °C/min up to 320 °C and 320 °C for 8 min. Between each sample and each standard solution, a run with DCM was made in order to clean the equipment.

The mass detector was operated in the electronic impact mode at 70 eV; transfer line temperature 300 °C and source temperature 320 °C. Full scan between 33 and 700 m/z for the qualitative analyses and selected ion monitoring (SIM) mode according to Table 1 for the selected phthalates.

Results and Discussion

Method performance

Figure 1 shows a chromatogram of the calibration solution: the total ion current (TIC) and extracted-ion chromatograms according to each phthalate. The main parameters of the method performance: limit of detection (LOD), limit of quantification (LOQ) and linear range are reported in Table 2 for each phthalate. A good linearity of response was achieved in the range considered. The coefficients of determination (R^2) were higher than 0,999 for all phthalates. LOD and LOQ were calculated from the calibration curve, as 3 and 10 times the standard deviation of the intercept, respectively and, when transformed into the bib concentration base, were in the order 0.1 to 0.2 $mgkg^{-1}$ for all phthalates except for DEHP, DINP and DIDP for which the values ranged between 0.3 and 0.6 $mgkg^{-1}$.

Phthalates quantification in bibs

The phthalates concentration in bibs are shown in Table 3. The values are expressed as concentration in $mgkg^{-1}$ bib ± standard deviation. A multi-factor ANOVA was performed (Fisher Least Significant Difference; p-value <0.05; different letters in the same column mean significant differences).

The most frequently detected phthalates were DBP and DIBP, in nearly all samples, and DEP and BBP in 16 out of 22 samples. The highest levels were detected for BPP, with 6 samples presenting concentration from 13 to 47 $mgkg^{-1}$ and one sample with the highest value of 65 $mgkg^{-1}$. DIBP was quantified in one sample at 30 $mgkg^{-1}$. DBP and DEP concentration averaged around 2 $mgkg^{-1}$. DEHP was detected in 6 samples, with values up to 24 $mgkg^{-1}$.

It seems there is a fair correlation between DIBP and DBP (Pearson coefficient 0.895), with concentration values for DIBP always higher than the ones for DBP in most samples (Figure 2). This seems to suggest the intended use of DIBP either in the main plastic or in the printing inks in spite of being not authorized in plastics FCM, according to European harmonized legislation for plastics. It is neither authorized in printing inks, according to Swiss legislation (FSVO, 2019). DIBP is authorized by U.S. Food and Drug Administration (FDA) in adhesives to be used (i) separated from the food by a functional barrier, (ii) in dry foods or (iii) when in contact with fatty and aqueous foods only through edges and seams of laminates. DIBP is also addressed in the German BfR Recommendations on Food Contact Materials to be used in plasticizer-free PVC and copolymers and in unsaturated polyester resins but only as pasting agent for catalysts (BfR, 2019) and with the same restrictions applicable to DBP in accordance with the Reg. (EU) No 10/2011 (EU, 2011). Recently, the European Food Safety Authority (EFSA) updated its opinions published in 2005 on DBP, BBP, DEHP, DINP and DIDP authorised for use as plasticisers and technical support agents in plastic for food contact (EFSA, 2019). However, EFSA did not consider DIBP because it is not authorised for use in plastic FCM. Nevertheless, EFSA recognized that DIBP can substantially add to the overall exposure of consumers to phthalates because of similar intake estimates compared to DBP. Furthermore, biomonitoring studies have indicated a trend towards increased human exposure to DIBP as a consequence of replacement for DBP (Zota et al. 2014). Therefore, it is worthy to note that the use of DIBP in FCMs and consequent exposure should be better characterized in spite of being a phthalate not authorized for food contact.

DHP and DNOP were not detected in any of the samples analysed and DMP was detected in one sample at low level. DAP was detected in 2 samples out of 22, in one sample at ca 1 $mgkg^{-1}$ and in another sample at a level of 5 $mgkg^{-1}$. This result may also be worthy to further develop because DAP has a migration level that should be non-detectable. DINP was detected in 3 samples with the highest concentration of 7 $mgkg^{-1}$ and DIDP was detected in one sample only at 2.5 $mgkg^{-1}$.

Phthalates migration estimates

The results of phthalates concentration in the bibs were then translated into the migration assuming a total mass transfer and the conventional ratio of 6 dm^2 kg^{-1} food. These are shown in Figure 3 as a radar plot of the concentrations (after normalizing with logarithms of the concentration values). Each line represents a bib sample and a comparison is made with the specific migration limits reported in Regulation (EC) No 10/2011 (black dotted line).

Worst case migration estimates for BBP are well below the SML (30 $mgkg^{-1}$) for all samples and the same applies to DBP (0.3 $mgkg^{-1}$), DEHP (1.5 $mgkg^{-1}$), DINP and DIDP (sum 9 $mgkg^{-1}$). The non-authorised phthalates DMP, DHP and DNOP also have worst-case estimated migration levels lower than the applicable limit of 0.01 $mgkg^{-1}$ for all bibs tested.

The worst-case estimated migration for DEP and for DIBP, which are non-authorised phthalates, exceed the applicable value of 0.01 $mgkg^{-1}$ in 9 and 16 out of 22 samples, respectively. The maximum estimated migration was 0.1 $mgkg^{-1}$ for DEP and 0.24 $mgkg^{-1}$ for DIBP and both occurred in one sample only.

As indicated, DIBP was the phthalate with higher number of undue occurrences and also showing the highest levels of estimated migration. A recent systematic review, corroborating previous studies, provided evidence that DIBP causes male reproductive and developmental toxicity and slight evidence for female reproductive toxicity, among other effects, supporting DIBP as a children's health concern (Yost et al., 2019). Furthermore, studies on the association of early life exposure to metabolites of several phthalates, including DBP and DIBP, with obesity and cardiovascular risks in childhood suggest that early life exposure may affect child growth and adiposity - mono-isobutyl phthalate (MiBP), the metabolite of DIBP was associated with higher total cholesterol levels at 4–6 years (Vafeiadi et al., 2018).

Calculated values for migration are recognized to overestimate the real migration values, but nevertheless are indicative of the need for surveillance particularly because bibs are often wrongly not seen by industry as food contact materials, and surveillance actions are not systematically acted. In fact, the nature of use of the article in question (baby bibs) is relatively uncertain regarding the contact conditions that affect migration, namely regarding the time of use. Temperature of contact can be well estimated as this is not much different than the baby body temperature. The time of contact depends on the frequency and duration of meals but the practice of keeping the bib on the baby between meals is not uncommon (Rajbux et al, 2020). According to the JRC Guidelines on testing conditions for articles in contact with foodstuffs (Beldi et al., 2019), the migration test would be performed with simulants A (10% ethanol v/v), B (3% acetic acid (w/v) and D2 (vegetable oil), with 0.5 hours of contact at 40 °C and under repeat use conditions. However, it is well known that most often babies were the bib for much longer time and they chew and suck the material, therefore increasing the potential for intake of migrants.

Conclusions

This work focused on screening plastic baby bibs to detect and identify phthalates and to determine their potential migration. Results indicate that several non-authorised phthalates are being used either in the plastic or in the printing inks. The most frequently phthalates detected were DBP and DIBP, the latter present often in higher concentration than the first one, suggesting its intended use. Worst case migration calculations indicate that DEP, DAP and DIBP exceed the 0.01 $mgkg^{-1}$, and therefore, determination of experimental migration is needed to conclude on compliance of baby bibs with the European and Swiss legislation. Bibs are considered, accordingly to European legislation, as FCMs and therefore, they should comply with the applicable rules, restrictions and limits. These articles should be included in surveillance plans, focusing in monitoring bibs composition, migration and the application by industry of good manufacturing practices.

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