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Migration of epoxidized soybean oil (ESBO) and phthalates from twist closures into food and enforcement of the overall migration limit

Abstract

Nineteen samples of food in glass jars with twist closures were collected by the national food inspectors at Danish food producers and importers, focusing on fatty foods, such as vegetables in oil, herring in dressing or pickle, soft spreadable cheese, cream, dressings, peanut butter, sauces and infant food. The composition of the plasticizers in the gaskets was analyzed by GC-FID and GC-MS. Epoxidized soybean oil (ESBO) and phthalates were determined in the homogenized food samples. ESBO was the principal plasticizer in five of the gaskets; phthalates in the remaining fourteen. ESBO was found in seven of the food samples at concentrations from 6 to 100 mg/kg. The highest levels (91 – 100 mg/kg) were in oily foods like garlic, chilli or olives in oil. Phthalates, i.e. di-iso-decylphthalate (DIDP) and di-iso-nonylphthalates (DINP) were found in seven samples at levels of 6 to 173 mg/kg. The highest concentrations (99 –173 mg/kg) were in products of garlic and tomatoes in oil and in fatty food products like sauce béarnaise and peanut butter. For five of the samples the overall migration from unused lids to the official fatty food simulant olive oil was determined and compared to the legal limit of 60 mg/kg. The results ranged from 76 to 519 mg/kg and as a consequence the products were withdrawn from the market.

Keywords: ESBO, phthalates, gaskets, migration, enforcement.

Introduction

Glass jars with metal twist closures are widely used for a broad range of foodstuffs, such as infant foods, pickled herrings, vegetables in oil or water, sauces, peanut butter, milk products, soft cheese products, pesto etc. Many of these products are intended for storage up to two years and in order to ensure a long shelf life, a plasticized PVC gasket is placed inside the closures to form an airtight seal against the rim of the jar. Several of these foodstuffs are pasteurized or sterilized in the glass containers at high temperatures. Several studies have reported that ESBO is frequently used as plasticizer and as a scavenger of hydrochloric acid in PVC gaskets (Hammarling et al., 1998; Fantoni et al., 2003; Fankhauser-Noti et al, 2005a). The gasket material contains typically about 25-40 % plasticizer and consequently a substantial migration to the food can take place (Biedermann-Brem et al., 2005b). The migration of ESBO into fatty foods, like food rich in edible oil, has been shown to be high (Fankhauser-Noti et al., 2005).

ESBO is on the positive list in the EU plastics directive (EC, 2002) and a specific migration limit for ESBO of 60 mg/kg is derived from the tolerable daily intake (TDI) of 1 mg/kg body weight/day (European Commission, 2005) set by the European Food Safety Authority (EFSA). This limit, which is identical to the overall migration limit, was far exceeded for many fatty and oily foods and even for food with a fat content as low as 4 % free oil or fat (Fankhauser-Noti and Grob 2006a and b). Therefore, to clarify the legal situation an interim migration limit, valid until 30 June 2008, of 300 mg ESBO/kg fatty foodis in force (EC 2007a). The Commissions risk management was based on exposure calculations from the European Food Safety Authority (EFSA, 2006). However, for infant foods the Commission has introduced a specific migration limit (SML) of 30 mg/kg food (EC, 2007a), taking into account that for infants of age 6-12 month the TDI of 1 mg/kg bw/day can easily be exceeded by a factor of up to 4 or 5 already with a limit of 60 mg/kg. A previous study (Fantoni et al., 2003) showed that some 15 % of the infant foods collected from the markets of various European Union Member States contained more than 30 mg ESBO/kg . In the study, surprisingly, no correlation between the migration of this lipophilic compound and the fat content of the samples was seen.

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5 It is well known from several studies that a migration of phthalates plasticizers from packaging
6 materials into fatty food can take place (Petersen et al., 2000; Sharman et al., 1994; Page et al.,
7 1992). Much public attention has been paid to phthalates since animal studies indicate that adverse
8 effects on human reproduction could be foreseen to occur when exposed to such substances.
9 Therefore the use of these chemicals in the packaging industry was expected to decrease these years
10 through substitution with other plasticizers. However, until recently only little attention has been
11 paid to the possible use of phthalates in PVC gaskets. A Japanese study found that DEHP, DINP
12 and DIDP were used as plasticizers in cap sealing resins of imported bottled food including
13 foodstuffs produced in Europe (Hirayama K., et al., 2001). Recent studies have confirmed that
14 phthalates are used in gaskets coming into contact with different kinds of food (Fankhauser-Noti et
15 al., 2006a; Fankhauser-Noti and Grob 2006b). From these studies it seems that the migration of
16 phthalates (percentage of plasticizer migrating from the gasket material in food contact) is higher
17 than for ESBO.
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29 The TDI's for di-n-butylphthalate (DBP), butylbenzylphthalate (BBP), di-2-(ethylhexyl) phthalate
30 (DEHP), (di-isononyl-phthalate (DINP) and di-iso-decyl-phthalate (DIDP) have been re-evaluated
31 by EFSA (EFSA, 2005). The EFSA risk assessments together with considerations about human
32 exposure from environmental sources (beside the contribution coming from food contact materials)
33 are transformed into specific migration limits by the 4. amendment to the plastics directive .
34 Furthermore, this amendment, beside introducing SML's for the phthalates DBP, BBP, DEHP,
35 DINP and DIDP, also requests that some of these shall not be used as plasticizers in single use
36 articles in contact with fatty food (EC, 2007 b).
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45 The aim of this project was to study the level of plasticizers migrating to selected foods packed in
46 glass jars with twist closures. The study included: Evaluation of the quality of compliance
47 documentation in the food industry, specific analysis of ESBO and phthalate migration (at the
48 official food control authority of the canton of Zürich, Switzerland) and control of the overall
49 migration limit by migration testing of unused lids (only were a high specific migration of
50 plasticizers was seen). In order to get packed foodstuffs as well as identical new/unused lids, most
51 of the samples came from Danish food producers/fillers. The intention was to gain a first impression
52 of the situation with these products on the Danish market, therefore only a limited number of
53 samples were included.
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Materials and Methods

Samples

Sample material. 19 samples of different kinds of food packed in glass jars with twist closures were sampled at Danish food producers and importers by the regional food control centres. The samples included oily products like tomatoes, olives, garlic and shrimps in oil, herring in pickle and dressing, milk products, soft spreadable cheese, sauces, peanut butter and infant food (mixed dishes of vegetables, rice and meat). All samples were taken in November 2004. Best before-dates for the products ranged from December 2004 (shrimps in oil with only one month of shelf life) to November 2006. Age of the products at sampling time is given in table 1. For each sample, three identical packagings were taken. In addition the corresponding new/unused glass jars and lids of the same kind were taken when available.

Compliance documentation. Documentation containing results from migration testing or equivalent compliance testing was collected by the food inspectors when available from producers of lids and food in supplement to the sampling.

Analytical methods

Identification of plasticizers in gaskets of lids. The additives in the PVC gasket were analyzed as described by Biedermann-Brem et al., 2005.b. Briefly, some gasket material from outside food contact was dissolved in tetrahydrofurane (THF). After precipitation of the PVC, the supernatant was analysed directly by GC-FID (for phthalates, Di-(2-ethylhexyl)adipate (DEHA) and Dibutylsebacate (DBS) and after transesterification to ethyl esters (for ESBO).

Infrared spectra of gaskets. Selected samples were analysed to verify the identity of major constituents of the gaskets (the polymer and the primary plasticizer) using a Fourier Transform Infrared Spectrometer (FTIR), in supplement to the analysis of extracts by GC-FID. The IR spectra were recorded by a Perkin Elmer Spectrum One FTIR Spectrometer with an Attenuated Total Reflectance (ATR) accessory with diamond interface. The spectra were obtained at 550-4000 cm^{-1} using a resolution of 4 cm^{-1} . Digital library spectra (Hummel- Scholl, 1999) as well as an Atlas of Plastic Additives Spectra (Hummel, 2002) were used when identifying the sample spectra.

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Preparation of food samples. The content of three jars of a given product was pooled and homogenised for 2-5 min in a blender. For heering in pickle the fish was drained before homogenising the fish meat. For food products in oil, the oil was separated from the solid food before homogenising the solid fraction; the food and the oil were weighed and analyzed separately.

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ESBO in food. ESBO was analyzed by the method described by Fankhauser-Noti et al, 2005. Briefly, homogenised food or oil was transesterified to methyl esters without prior extraction of the ESBO, using conditions avoiding saponification. Methyl esters were analysed by on-line LC-GC-FID. Transfer of the fraction containing the methyl esters of the diepoxy linoleic acid, involved concurrent eluent evaporation and a loop-type interface. The detection limit ranged from 1-3 mg/kg food and the relative standard deviation from repeated analyses was below 10 %. The recovery was 94-103 %.

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Samples with ESBO levels above the detection limit were analysed in duplicate. When the food and the oil were analyzed separately, the ESBO concentration in the product was calculated weighing the concentrations in the two fractions by the weight proportion of the fractions.

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Phthalates in food. The determination of phthalates in food involved GC-MS with injector-internal thermal desorption as described by Biedermann et al., 2005a and Fiselier et al, 2005. In brief, diluted oil or raw food extracts in n-butyl acetate were injected in splitless mode under conditions desorbing the phthalates from the oil layer deposited onto the wall of the injector liner. A precolumn coated with a thin film of stationary phase was backflushed towards the end of each analysis. The limit of detection was largely determined by the blanks and was below 1 mg/kg. MS involved electron impact ionization and selected ion monitoring. The recovery from spiked samples was better than 85 % and the measuring uncertainty was mostly below 20 %.

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Overall migration testing of lids. Testing of overall migration from lids was done by accredited analysis using test conditions according to the relevant directives (82/711 EEC and its amendments; 85/572/EEC) (EC, 1982; EC, 1985) and the European standard EN 1186 part 1 and 8 (CEN, 2002a; CEN 2002b). Unused glass jars with lids (from identical batches) used for the fatty food samples were filled with 100 ml of olive oil (sample 11-14 and 16). For those products, where a heating step

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4 is a part of the production process, the olive oil was heated up to the relevant temperature before
5 filling the jars with the fatty food simulant. After filling the simulant into the jars, they were closed
6 with the corresponding lid. The lids were exposed to olive oil by inverting the samples and kept at
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8 with the corresponding lid. The lids were exposed to olive oil by inverting the samples and kept at
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10 10 days at 40 °C. The overall migration from each lid were analysed according to EN 1186. In each
11 analytical series at least one sample was determined by a four double determination. For samples,
12 where quadruplicate analysis were made the results were well within the specified analytical
13 tolerance of the method (CEN, 2002a; CEN 2002b).
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21 Results

22 *Composition of plasticizers in the gasket of lids*

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24 Results in table 1 show that in 5 (26 %) of the samples, ESBO was used as principal plasticizer
25 constituting 28-33 % of the gasket material. In two of these samples (sample 18 and 19) ESBO was
26 used alone whereas in three samples (sample 12, 13 and 14) low levels of DBS was found in
27 addition. In the remaining 14 samples (74 %) phthalates were used as principal plasticizer in
28 combination with ESBO. DIDP were used in 10 of the gaskets at a level of 24-29 % in combination
29 with low levels of ESBO and in two cases (sample 6 and 10) low levels of DEHA and
30 DEHA/DEHP. In two of the gaskets (sample 3 and 16) DINP was the principal plasticizer in
31 combination with low levels of ESBO and DEHP (sample 3). Gaskets used with two of the dairy
32 products (sample 1 and 2) contained DEHP at a level of 31 %.
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41 “[Insert table 1 about here]”
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45 Results from FTIR analysis of the unused gasket material are represented by two samples with
46 respectively ESBO and phthalates as principal plasticizer. IR spectra of the two types of samples are
47 shown in figure 1 where the characteristic wavenumbers for the plasticizers are annotated.
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52 “[Insert figure 1 about here]”
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56 *Specific migration of plasticizers to foodstuffs*

57 The plasticizer levels found in foodstuffs are presented in table 2. Three of the five samples (sample
58 12, 13 and 14) with a high content of ESBO in the lids gave rise to high levels of ESBO in the food.
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These three samples were oily foods with fatty contact to the lid. The infant food samples (sample 18 and 19) were low in ESBO with a level below the detection limit. The declared level of fat in these products was 2-3 %.

The phthalates DIDP and DINP were found in seven food samples in a level above the detection limit of 1 mg/kg. In five of these samples, the levels of DIDP or DINP in the foodstuffs were higher than the SML's of 9 mg/kg (calculated from the TDI's of 0.15 mg/kg bw/day (EFSA, 2005) using the conventional factors of 60 kg body weight and 1 kg of food consumed per day). These products included oily products (tomatoes and garlic in oil), peanut butter, sauce béarnaise, and one product of herring in aqueous pickle. The highest levels of phthalates were found in the oily food products and in peanut butter with a declared fat content above 50 %.

“[Insert table 2 about here]”

Overall migration to the food simulant olive oil

For samples of oily and fatty foods showing a high migration of ESBO and/or phthalates from the lid into food, additional testing of overall migration from the lids was done. New/unused lids were however, not available for all samples. The overall migration result for the food simulant was calculated by dividing mg migrants per lid with the sample weight of a given sample. All results (in mg/kg food) were above the overall migration limit of 60 mg/kg according to table 2.

Compliance documentation

The documentation provided by the producers of lids and food included certificates of analysis from migration testing. In general the collected certificates contained information on overall migration testing of the plasticized PVC sealing. For a part of the samples additional test results from specific analysis of vinylchloride monomer or a few other specific substances were included. Only in a few cases migration testing of one or two phthalates was included in the compliance documentation, however, there were no tests for other plasticizers in the certificates. In general the testing was done on the sealing polymer and the results were expressed in mg/dm² of lining. Migration into food was estimated based on calculations assuming a certain surface-weight ratio.

Discussion

Compositional analysis of the gaskets by FTIR showed that due to the characteristic absorption bands of phthalates and ESBO respectively, it might be possible to distinguish between lids with ESBO as the principal plasticizer and those with phthalates as the principal plasticizers. FTIR analysis offer a quick initial semi-specific screening of the samples in order to decide which chemical analysis to be made on the food, in the food simulant or on the gasket material itself. This technique may possibly be useful in future compliance check for the presence of phthalates in the food contact material itself.

In five lids, ESBO was the principal gasket plasticizer, with a content of 28 – 33 %, whereas phthalates were the principal plasticizers in a majority of the gaskets (14 samples) with a relative content of 25-31 %. This distribution is different from what has been reported by others showing that ESBO is the most commonly used plasticizer in gaskets when studying oily foods and infant food products (Biedermann-Brem et al., 2005b, Frankhauser-Noti et al. 2006b). However, this difference may partly be due to the limited number of samples in this study.

ESBO concentrations in the food were above the SML of 60 mg/kg in three of the five samples (sample 12-14) with a high content of ESBO in the gaskets. For the remaining two samples (infant foods, sample no 18 and 19), the levels in the food were below the detection limit of 3 mg/kg. This is in spite of the fact that the level of ESBO in the gaskets was in the same range for all five samples (see table 1). One explanation might be that the fat content is much higher in samples 12-14 (oily products) compared to the fat content of the infant food samples (2-3% fat). However, a number of other parameters can affect the level of ESBO migration into food, including the following: Area and thickness of the gasket, area of gasket available for direct food contact, lid surface/sample volume ratio, the applied procedure of sterilization, date of analysis in relation to the production/expiry date of the product, consistency of the food and handling of the jar on its way from producer to consumer. These are all factors strongly influencing the extent of contact between food and gasket.

The results show that ESBO is easily extracted into edible oil and that migration levels above 60 mg/kg can be found even with products that are very recently produced, as the production dates of

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all three products were only one week before samples were taken into analysis. This is in support of the findings in a previous study (Fankhauser-Noti et al., 2005).

As seen from table 2, the level of phthalates in food vary greatly between samples with the same relative phthalate content in the gasket, possibly due to variations in the same parameters as given for ESBO above. The highest levels of phthalates were found in samples (sample 11, 15 and 16) of oily or fatty foods in relatively small jars (180 – 340 g food per jar) with rather high lid surface/sample volume ratio. In these products, the limit of 9 mg/kg for DINP/DIDP was exceeded by a factor of 10 to 19. Other products (béarnaise sauce and pickled herrings) have a lower content of phthalates in the food, but the levels were still above the limit of 9 mg/kg. As was the case for ESBO, the data show that phthalates are easily extracted into oily and fatty food within relative short time, as three of the products were taken into analysis within 1 – 3 month after the production date. Phthalates have only a limited solubility in water and aqueous media (Petersen et al., 2000) however, herrings contain much fat and some of this may be extracted into the aqueous pickle over time given an emulsion of water/fat. As an intimate contact between the pickle and the gasket is likely to occur, migration into the fish meat can be expected. The actual levels can be seen from table 2. Previous studies on oily products has shown that migration rate for DIDP and other phthalates far exceed migration rate of ESBO and that also migration from parts of the gasket not being in direct food contact take place due to a fast diffusion of the phthalates inside the PVC-plastics constituting the gaskets (Fankhauser-Noti, 2006a).

In this study the ratio between lid surface area (in dm^2) and sample weight (in kg) varies between samples within the range of 0.14 – 1.17 (dm^2/kg) as seen from table 1. The rather low lid surface/sample weight ratio for sample 10 (shrimps in oil, with a ratio of 0.37) is probably one important reason for the much lower concentration of phthalates in this product compared to e.g. sample 11 (garlic in oil, with a ratio of 1.00). Another observation from this study was that in samples where individual analyses of the solid food fraction and the oil fraction took place, the level of phthalates and ESBO in the oil fractions is several times higher than in the food fractions (results not shown).

Results of overall migration testing of the lids into the food simulant olive oil at 40 °C in 10 days were in the same order of magnitude as the sum of the measured specific migration of plasticisers

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4 into the food (or somewhat higher). Here the testing scheme ensures that an intimate contact
5 between the food simulant and the gasket occurs. It is not surprising that the values can be high as
6 the overall migration in this case is the sum of the concentration of all specific non-volatile
7 chemicals in the gaskets. Beside additional plasticizers, this may include e.g. slip agents in high
8 levels as found by Fankhauser et al., 2006b.
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15 An evaluation of the industry's compliance documentation indicated that the demands in Article 3
16 in Framework Regulation 1935/2004 (EC, 2004) was not respected. First of all, own-check
17 documentation was incomplete and even misleading in many cases due to missing data on specific
18 migrants of relevance and due to the applied principle of testing. Instead of testing the actual "ready
19 for use" gasket, the migration testing in the gasket materials producing industry is often performed
20 using a sample of the sealing compound without correcting for the specific lid surface- food weight
21 ratio in actual use. Furthermore, differences in thickness of the gasket material in the final material
22 and in the test specimen is ignored, as well as the diffusion of migrants, which is likely to occur
23 from parts of the gasket not being in direct contact with the food. Altogether, this may lead to a
24 serious underestimation of the migration. This observation underline the need for fulfilling the
25 requirements in legislation saying that migration testing should be done using worst-case test
26 conditions and preferably on the final article ready for use.
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38 The observation that phthalates were used as principal plasticizers in a majority of the gaskets
39 analysed in the project came as a surprise to the authors. The expectations were that these chemicals
40 would no longer be used in materials coming into contact with fatty foods, as in Denmark much
41 attention has been paid by authorities and the public to the negative impact of certain phthalates on
42 reproduction. For this reason, only limited awareness has been paid from enforcement bodies to the
43 potential use of these substances in PVC gaskets for food contact.
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50 All samples violating the overall migration limit were withdrawn from the market by the local food
51 inspectors. The Danish industry, including producers and importers of twist caps, food producers
52 and retailers, were informed about the problems by the Danish Veterinary and Food Administration.
53 Moreover the European Metal Closure Group was informed about the non-compliant lids as a
54 general problem and the immediate need for solutions. As a consequence of the observed problems,
55 the biggest retailers in Denmark strengthened their own check control in spring 2005. Due to the
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5 observed violation of the regulations it is the intension of the authorities to repeat the control
6 campaign on lids, by taking more samples of domestic and imported origin. Results from this
7 project (and from related projects in other European Countries) were already communicated to the
8 EC-Commission and legislative measures will be implemented in the member states during
9 2007/2008 (EC 2007 a and b).
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14 15 16 17 **Conclusion**

18 The lids taken into this study contained either ESBO or phthalates, like DIDP, DINP and DEHP as
19 the principal plasticizers. When the gaskets were used with fatty or oily food in small and medium
20 size glass jars, the level of migration of ESBO or phthalates violated several times the actual
21 migration limits in force at the time of sampling. In samples tested for overall migration the
22 migration level was at least in the same order of magnitude as the sum of specific migration of
23 ESBO and phthalates.
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31 In general the demands for safe and inert packaging materials, as required in article 3 in Regulation
32 1935/2004, was not fulfilled by the industry. Obviously the own-check documentation was not
33 based on realistic worst-case test conditions.
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- Di-Butylphthalate (DBP) for use in food contact materials

Question N° EFSA-Q-2003-192, Adopted on 23 June 2005 by written procedure

- Di-isodecylphthalate (DIDP) for use in food contact materials

Question N° EFSA-Q-2003-195, Adopted on 30 July 2005

- Di-isononylphthalate (DINP) for use in food contact materials

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Sample no.	Type of Food	Age of product at time of sampling (month)	Area of lid (dm ²)	Sample weight (g)	Ratio of lid surface-to weight of food (dm ² /kg)	Plasticizer composition of gasket polymer:					
						ESBO	DIDP	DINP	DEHP	DEHA	DBS
						(% w/w)	(% w/w)	(% w/w)	(% w/w)	(% w/w)	(% w/w)
1	Chocolate milk	< 1	0.06	420	0.14	4			31		
2	Cream	not given	0.06	200	0.30	3			31		
3	Soft cheese	1	0.28	240	1.17	10		24	2		
4	Dressing, crème fraiche	2	0.06	387	0.15	4	25				
5	Herring in dressing	not given	0.25	310	0.81	7	24				
6	Herring in pickle	not given	0.45	619	0.73	2	25		1	2	
7	Herring in pickle	not given	0.45	617	0.73	6	26				
8	Herring in pickle	not given	0.45	467	0.96	7	25				
9	Herring in pickle	not given	0.25	292	0.86	7	25				
10	Shrimps in oil	< 1	0.62	1665	0.37	2	25			3	
11	Garlic in oil	3	0.18	179	1.00	4	29				
12	Garlic/chilli in oil	< 1	0.18	184	0.98	32					2
13	Garlic in oil	< 1	0.18	181	0.99	33					2
14	Olive in oil	< 1	0.22	271	0.81	32					2
15	Tomatoes in oil	12	0.22	297	0.74	3	31				
16	Peanut butter	2	0.25	340	0.74	7		20			
17	Sauce bearnaise	< 1	0.25	334	0.75	7	25				
18	Infant food	not given	0.15	190	0.79	29					
19	Infant food	5	0.15	181	0.83	28					

Sample no.	Type of Food	ESBO in food (mg/kg)	Phthalates in food (mg/kg)	Phthalates identified in the food	Overall migration (mg/kg)
1	Chocolate milk	<3	<1		
2	Cream	<3	<1		
3	Soft cheese	<3	<1		
4	Dressing, creme fraiche	<3	<1		
5	Herring in dressing	<3	<1		
6	Herring in pickle	<3	8	DIDP	
7	Herring in pickle	<3	n.a.		
8	Herring in pickle	<3	24	DIDP	
9	Herring in pickle	<3	n.a.		
10	Shrimps in oil	<3	6	DIDP	
11	Garlic in oil	6	173	DIDP	519
12	Garlic/chilli in oil	91	n.a.		464
13	Garlic in oil	91	n.a.		470
14	Olives in oil	100	n.a.		267
15	Tomatoes in oil	6	126	DIDP	
16	Peanut butter	9	99	DINP	76
17	Sauce bearnaise	6	33	DIDP	
18	Infant food	<3	n.a.		
19	Infant food	<3	n.a.		

n.a.: not analysed

