Chapter 3
Plasticisers Used in PVC for Foods: Assessment of Specific Migration

Luciana Bolzoni

Abstract The use of polyvinyl chloride (PVC) in food packaging is mainly related to the plasticity of the same material when used in wrapping films and in gaskets for metal closures (applications: glass jars and bottles). Anyway, main required characteristics are the flexibility, the softness and the possibility of being used for wrapping films and hermetic closures. Pure PVC is a rigid material, but it may also be mixed in remarkable proportions with other substances: the final product may become flexible, soft and plastic. Many plasticisers may be used in the European Union in accordance with the Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food. In relation to food contact-approved PVC materials, inglobated plasticisers can gradually migrate from the plasticised object to foods depending on the influence of factors such as the temperature or the physical medium (solvent, food). The Regulation (EU) No. 10/2011 provides specific migration limits for different plasticisers. The analytical control of these limits in foods and/or in food simulants is important by the viewpoint of food safety. Currently available and used methods for the evaluation of specific migration are reviewed in this paper.

Keywords Gas chromatography · High-performance liquid chromatography · Mass spectrometry · Phthalate · Plasticiser · Polyvinyl chloride · QuEChERS · Specific migration limit

Abbreviations

acPG	Acetylated partial glycerides
AFC	Panel on food additives, flavouring, processing aids and materials in contact with food
ATBC	Acetyl tributyl citrate
BBP	Benzyl butyl phthalate
BBPd4	Benzyl butyl phthalate deuterated
DEHA	Bis-ethylhexyl adipate
DINCH	1,2-Cyclohexane dicarboxylic acid, diisononyl ester

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DBP	Dibutyl phthalate
DBPd4	Dibutyl phthalate deuterated
DBS	Dibutyl sebacate
DCP	Dicyclohexyl phthalate
DEHP	Di(2-ethylhexyl) phthalate
DEHPd4	Di(2-ethylhexyl) phthalate deuterated
DEP	Diethyl phthalate
DEPd4	Diethyl phthalate deuterated
DEHS	Di-2-ethylhexyl sebacate
DIBP	Diisobutyl phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DMG	Dimethyl glutarate
DMP	Dimethyl phthalate
DMPi	Dimethyl pimelate
DMS	Dimethyl sebacate
DPP	Di-*n*-propyl phthalate
DOP	Dioctyl phthalate
DOPd4	Dioctiyl phthalate deuterated
DpeP	Dipentyl phthalate
ESBO	Epoxidised soybean oil
EFSA	European Food Safety Authority
SSICA	Experimental Station for the Food Preserving Industry
FID	Flame ionisation detector
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
HPLC	High-performance liquid chromatography
LC	Liquid chromatography
LC/MS	Liquid chromatography/mass spectrometry
LC/MS/MS	Liquid chromatography/tandem mass spectrometry
MW	Molecular weight
$MgSO_4$	Magnesium sulphate
PVC	Polyvinyl chloride
PSA	Primary and secondary amines
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RPLC	Reversed-phase liquid chromatography
SML	Specific migration limit
THF	Tetrahydrofuran

3.1 Introduction

Polyvinyl chloride (PVC) is one of the most used materials in the world; the use of this polymer in the production of objects dates back to the first half of the twentieth century. The use of PVC in contact with foods—for example in pipes,

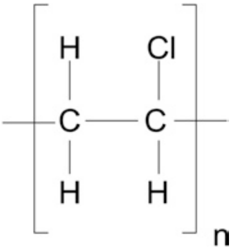

Fig. 3.1 Chemical structure of polyvinyl chloride (PVC). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

conveyor belts of food industry or in packaging materials—is mainly due to the intrinsic plasticity of the polymer. This feature, also named ‘flexibility’, and softness are fundamental features for the seals of caps, for the hermetic closure of glass jars and bottles when destined to contain foods. In particular, hermeticity is essential because of the need of assuring the sanitary safety of processed foods after thermal treatments such as pasteurisation or sterilisation.

Pure PVC (Fig. 3.1) is a rigid material, and it is used in several ways. In detail, PVC may be used alone in extrusion processes for the production of section bars (doors and windows, pipes, etc.). On the other side, PVC can be also mixed with plasticizing substances in high proportions. The final product may be softer, more flexible and with remarkable plastic properties if compared with a pure PVC object.

In relation to most used plasticisers for PVC, a peculiar group concerns polycarboxylic acids: phthalic acid esters, adipic acid esters, sebacic acid esters and so on, with alcohols of variable length.

By the chemical viewpoint, plasticisers can be inglobated in PVC because of the solvation of C–CI polar chemical bonds on the polymeric chain. The solvation is mainly due to carboxylic (COO^-) polar groups; should aromatic rings be attached to the chemical structure, the influence of π-electrons would be an additional factor. A physical bond is hence created between PVC and plasticisers; however, this bond cannot be confused with a chemical interaction. For this reason, the plasticizing agent can gradually migrate from food contact PVC surfaces into packaged foods in connection with concurring factors such as storage temperatures and/or the chemical and physical nature of the medium (solvent, food).

3.1.1 Phthalates

A group of plasticisers that has been repeatedly discussed in the last few years concerns phthalates. Essentially, they are phthalic acid esters (Fig. 3.2): some of these molecules are more used than others. As a consequence, the abundance of the scientific literature concerns only a limited subgroup of phthalates.

One of the most used phthalates (as PVC plasticizer) is di-2-ethylhexyl phthalate (DEHP). This molecule is a phthalic acid ester obtained with 2-ethylhexanol.

With reference to the human health, main doubts on this type of phthalates concern the role of DEHP as destroyer of the human endocrine system; in particular, detrimental effects of DEHP have been detected on the reproductive system [1].

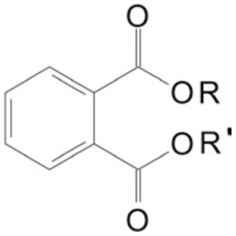

Fig. 3.2 General formula of phthalates. R e R' group can be equal. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

Several restrictions on DEHP and some phthalates have been introduced in the European Union since several years. In fact, the use of phthalates is not allowed with concentrations higher than 0.1 %, neither in toys nor in childhood products; the reason of this restriction is due to exposure hazards that can originate from chewing or sucking such objects for a long time [2].

Some restrictions also include materials that are in contact with food. The Regulation (EU) No. 10/2011 [3] defines restrictions for the use and specific migration limits (SML) for some types of phthalates on the basis of the tolerable daily intake (TDI) [1, 4–7]:

- Benzyl butyl phthalate (BBP)
- Dibutyl phthalate (DBP)
- Diisodecyl phthalate (DIDP)
- Diisononyl phthalate (DINP)
- DEHP.

Other phthalates are not taken into account such as diisobutyl phthalate (DIBP): this substance is widely used and, therefore, easily detectable in analytical samples and blanks.

Consequently, SML values lower than 0.010 mg/kg are accepted, according to the Regulation No. 10/2011, for substances which are not included in Annex I.

3.1.2 Epoxidised Soybean Oil

Epoxidised soybean oil (ESBO) (Fig. 3.3) is widely used as an alternative to phthalates because of similar features in relation to plasticizing effects. Moreover, ESBO can also act as a scavenger for hydrochloric acid, which is released from PVC during heat treatments of PVC-based materials. For this reason, ESBO is definable as a 'decontaminating' agent when used in connection in PVC.

However, ESBO is highly lipophilic: the notable attitude to migration (or release from organic supports) of this natural origin plasticiser has been outlined about 10 years ago. In relation to available studies, two researches—an European study on baby foods [8] and other tests on oily foods in jars—have to be mentioned [9]. In detail, the release of ESBO in oils after the free contact between

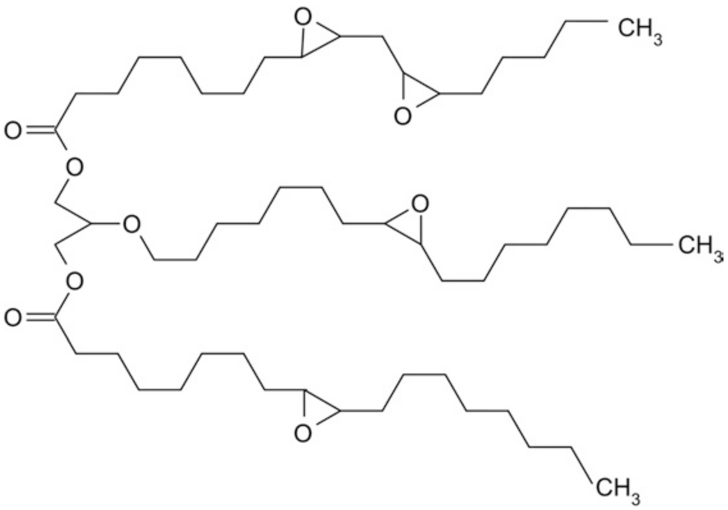

Fig. 3.3 Chemical structure of epoxidised soybean oil (*ESBO*). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

foods and plasticized materials (ESBO was the only plasticizing agents) led SML and global limits to notable levels.

After the evaluation of the European Food Safety Authority (EFSA), the European Community has established a SML value of 30 mg/kg for baby food. On the other side, SML has been raised to 300 mg/kg for other foods in relation to ESBO for a limited period. The main reason was correlated to the temporal implementation: in other words, manufacturers of films and sealing compounds should have been reasonably able to find other plasticisers and formulations within a specified deadline. Subsequently, a SML value of 60 mg/kg, which is still effective, has been established [3].

3.1.3 Other Monomeric Plasticisers

Acetyl tributyl citrate (ATBC) (Fig. 3.4) is a common plasticiser for food contact applications. This molecule shows an excellent biodegradability and a chemically remarkable affinity to PVC because of the polarity. The Regulation (EU) No. 10/2011 does not report SML values for ATBC; consequently, a general SML of 60 mg/kg is considered. However, ATBC is also highly soluble in lipophilic materials and, therefore, highly soluble in them. Sebacates are also considered good plasticisers, and their moderate toxicity is known at present; on the other hand, dibutyl sebacate (DBS) (Fig. 3.5) only is currently reported in the 'positive list' of the Regulation (EU) No. 10/2011 without limits of specific migration for food contact applications (SML = 60 mg/kg).

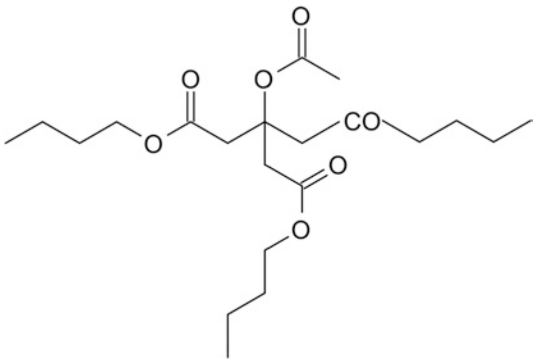

Fig. 3.4 Chemical structure of acetyl tributyl citrate (*ATBC*). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

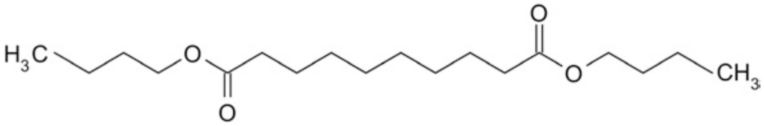

Fig. 3.5 Chemical structure of dibutyl sebacate (*DBS*). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

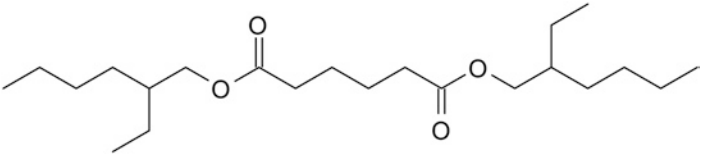

Fig. 3.6 Chemical structure of bis-ethylhexyl adipate (*DEHA*). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

Another widely used plasticiser is bis-ethylhexyl adipate (DEHA) (Fig. 3.6); the above-mentioned Reg. No 10/2011 defines a SML values for DEHA of 18 mg/kg on the basis of the opinion of the Scientific Committee on Food in 2000 [10].

1,2-Cyclohexane dicarboxylic acid, diisononyl ester (DINCH) (Fig. 3.7) is currently considered the non-aromatic alternative to phthalates [11] and to DEHP in particular. However, DINCH is reported to show a high migration tendency when in contact with oily foods. Some acetylated partial glycerides (acPG)—monoglycerides and diglycerides—are employed as plasticisers, for example, glyceril monolaurate diacetate, glyceril dilaurate monoacetate hydrogenated castor oil with glycerine and acetic acid (ARMG). In relation to acPG, the Regulation (EU) No. 10/2011 does not impose a SML value; as a result, the limit of 60 mg/kg is considered. acPG are considered as plasticisers without particular safety consequences because of their

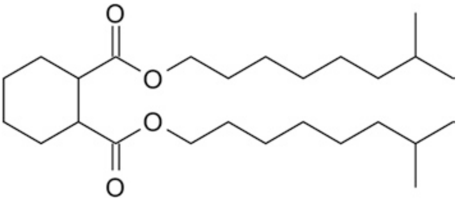

Fig. 3.7 Chemical structure of 1,2-cyclohexane dicarboxylic acid diisononyl ester (*DINCH*). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

chemical similarity to natural raw materials. The presence of long alkyl chains is the main cause of the notable solubility of acPG in non-polar solvents; therefore, a potentially high migration in oil can be hypothesised.

3.1.4 Polyadipates

Monomeric plasticisers have been replaced at least partly by polymeric plasticisers. In particular, polyadipates are considered as good options: their high molecular weight does not help migration. However, molecules up to 1,000 Da migrate more easily, and a migration limit of 30 mg/kg has been defined for these situations, on condition that polyadipates are authorised by the Reg. No 10/2011. Figure 3.8 shows some structural elements of polyadipates [3].

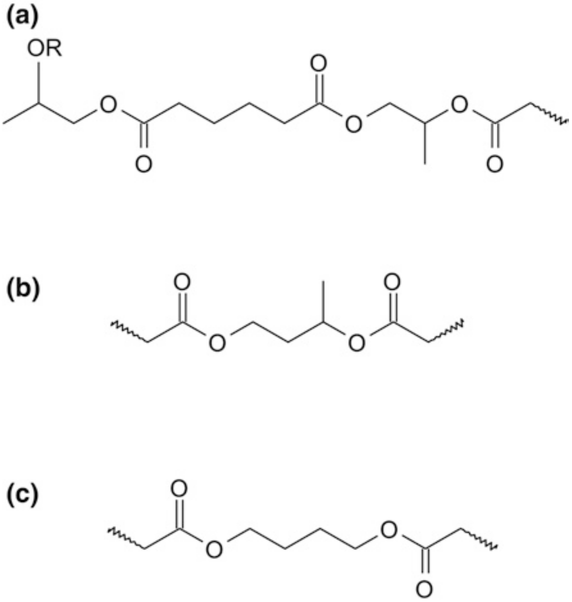

Fig. 3.8 Structural elements of polyadipates: 1,2-propanediol adipate (**a**), 1,3-butanediol adipate (**b**) and 1,4-butanediol adipate (**c**). BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing these structures

3.2 Analytical Controls of Specific Migration Limits in Foods and Food Simulants

As already outlined for all the mentioned plasticisers, some SML values are required by the Regulation (EU) No. 10/2011. These numerical restrictions are referred to food products for the whole commercial life. SML must be checked and estimated also in simulant liquids on condition that the material has not been yet in contact with the food, and contact conditions are established in the Chap. 2 of Annex V of the Regulation [3].

Consequently, there is the necessity of available laboratories committed to the control and the verification of food safety in relation to packaged foods and packaging materials containing plasticisers. In detail, the creation and the implementation of reliable analytical methods for the analysis of plasticisers in packaging materials is needed. On the basis of chemical features of above-mentioned substances, the most important food matrices are obviously oily foods including the ‘D simulant’ (oil) [3]. By the analytical viewpoint, the main reason is correlated to observed releases: the migration is higher towards oil, greasy and oily foods.

3.2.1 Methods for the Analysis of Phthalates

Published methods are based, for the most part, on the instrumental determination in gas chromatography/mass spectrometry (GC/MS) after extraction or purification of the extract.

The extraction is often carried out with low polar solvents, and plasticisers are extracted together with lipid substances from which they have to be separated before gas chromatography (GC) determination. To this aim, gel permeation chromatography has been used [12]. Direct injection without purification has successfully been used, using a special GC injector with inner thermal desorption and external discharge of lipid substances [13].

The extraction can also be carried out with polar solvents such as methanol or acetonitrile with less co-extracted lipid substances; however, a purification step is necessary even in this situation [14]. At present, new methods based on the determination in liquid chromatography/tandem mass spectrometry (LC/MS/MS) and also liquid chromatography/mass spectrometry (LC/MS) with high resolution are available [15, 16].

This work would also describe two procedures for the determination of phthalates. These methods are currently used at the Experimental Station for the Food Preserving Industry (SSICA) in Parma, Italy. The first procedure is based essentially on the method developed by Sannino [17] which requires the extraction in acetonitrile and the subsequent purification on a Florisil column, while the second system is based on the preparation of the sample with the ‘Quick, Easy, Cheap, Effective, Rugged and Safe’ (QuEChERS) method.

The QuEChERS method is an easy and effective technique for the multi-residual analysis of pesticides in food, allowing also the considerable reduction of time and costs [18]. This procedure has been tested at SSICA for the analysis of phthalates in oil and products in oil.

3.2.2 QuEChERS Method: A Case Study

The preparation of food samples with the QuEChERS method has been schematically reported in Table 3.1. This section concerns the description of a normal determination of phthalates in oils and anchovies in oils at SSICA.

In relation to this research, the instrumental determination has been based on a triple quadrupole GC/MS system in series. The used column has been a Phenomenex Guardian^{TM} column (30 m × 0.25 mm inner diameter; film thickness 0.25 μm) with following conditions: injection temperature: 250 °C; source temperature: 230 °C; transfer line temperature: 300 °C. Table 3.2 shows analysed phthalates and deuterated phthalates used as internal standards. In addition, chromatograms of a standard mixture of analysed phthalates and of used internal deuterated standards phthalates have been reported in Figs. 3.9 and 3.10.

Ten recovery trials have been tested in oil and anchovies in oil at the 0.5 mg/kg fortification level for all phthalates except for DEHP and dioctyl phthalate (DOP) with 1 mg/kg and DIDP with 10 mg/kg.

Mean per cent recoveries have been higher than 77 % in oil with the exception of dicyclohexyl phthalate (DCP) and DIDP with 60 %. With concern to anchovies in oil, all recoveries have been higher than 73 %.

Table 3.1 A QuEChERS method scheme

Step number	Description
Step 1	Weight 5 g of homogenised sample
Step 2	Add internal standards and 10 ml of acetonitrile. Shake for 1 min
Step 3	Add the extraction salt: 4 g of magnesium sulphate ($MgSO_4$) + 1 g of sodium chloride + 1 g of trisodium citrate dehydrate + 0.5 g of disodium hydrogen citrate. Shake for 1 min
Step 4	Centrifuge for 5 min at 4,000 rpm
Step 5	Transfer 6 ml in the test tube for the purification of vegetal matrices containing 25 mg primary and secondary amines (PSA) and 150 mg of $MgSO_4$. Should fat matrices be analysed, transfer 6 ml in the test tube for the purification of matrices containing 150 mg of PSA, 150 mg of C18 sorbent and 900 mg of $MgSO_4$
Step 6	Shake with vortex for 1 min
Step 7	Centrifuge for 5 min at 4,000 rpm Transfer in vial for the analysis in GC/MS

This procedure is used at SSICA with concern to the preparation of samples for the subsequent analysis of phthalates

Table 3.2 Phthalates and deuterated phthalates

Phthalates	Precursor ions (m/z)	Product ions (m/z)
Dimethyl phthalate (DMP)	163	133 + 135 + 105
Diethyl phthalate (DEP)	149	65 + 93 + 121
Diethyl phthalate deuterated (DEPd4)	153	69 + 97 + 125
Di-*n*-propyl phthalate (DPP)	149	65 + 93 + 121
Diisobutyl phthalate (DIBP)	149	65 + 93 + 121
Dibutyl phthalate (DBP)	149	65 + 93 + 121
Dipentyl phthalate (DpeP)	149	65 + 93 + 121
Dibutyl phthalate deuterated (DBPd4)	153	69 + 97 + 125
Benzyl butyl phthalate (BBP)	149	65 + 93 + 121
Dicyclohexyl phthalate (DCP)	149	65 + 93 + 121
Benzyl butyl phthalate deuterated (BBPd4)	153	69 + 97 + 125
Di(2-ethylhexyl)phthalate (DEHP)	149	65 + 93 + 121
Di(2-ethylhexyl)phthalate deuterated (DEHPd4)	153	69 + 97 + 125
Dioctyl phthalate (DOP)	149	65 + 93 + 121
Diisononyl phthalate (DINP)	149	65 + 93 + 121
Diisodecyl phthalate (DIDP)	149	65 + 93 + 121
Dioctyl phthalate deuterated (DOPd4)	153	69 + 97 + 125

Precursor ions and product ions

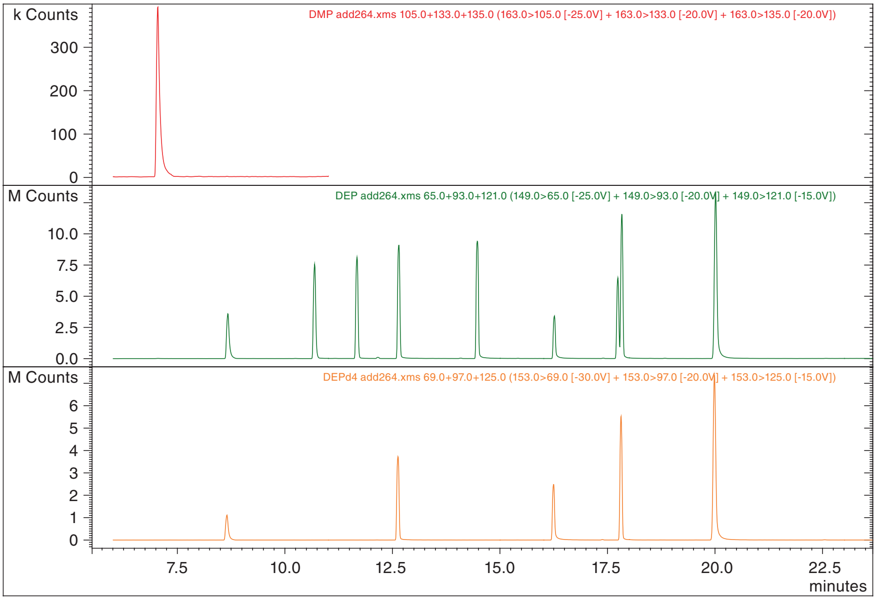

Fig. 3.9 Chromatograms of product ions used for the quantification: mixture of standard phthalates. In order: DMP (*red line*), DEP, DPP,DIBP, DBP, DPeP, BBP, DCP, DEHP, DOP (*green line*), DEPd4, DBPd4, BBPd4, DEHPd4 and DOPd4 (*orange line*)

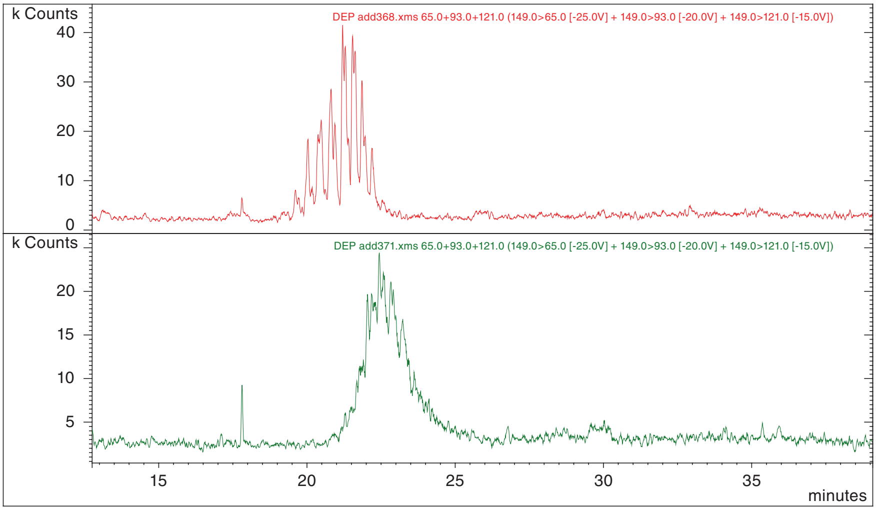

Fig. 3.10 Chromatograms of DINP (*red line*) and DIDP (*green line*) standards

Measured relative standard deviations for all analysed phthalates have been lower than 7.5 and 17 % in oil and anchovies in oil, respectively.

3.2.3 Analysis Methods for ATBC, DBS, DEHA, DINCH, Mono and Partially Acetated Diglycerides of Fatty Acids

Usually, methods used for the analysis of phthalates in foods can be also chosen when speaking of other non-polymeric plasticisers such as ATBC, DBS, di-2-ethylhexyl sebacate (DEHS), DEHA, DINCH and acPG.

Complex mixtures of non-polymeric plasticisers—including phthalates, DEHA, DINCH, DBS, ATBC, DEHS, glycerol monolaurate acetate and mono glyceryl myristate—can be determined in GC/MS with thermal desorption injector [13].

It has been reported also that the method of analysis of phthalates can be used with success when speaking of DBS, ATBC, DEHA and DINCH [17]. This procedure has been later modified in the clean-up step by means of the elution with more polar solvents in order to determine also acPG [17]. In Fig. 3.11 are reported GC/MS chromatograms of eight monomeric plasticisers in oil.

On the other side, recoveries are not suitable for all these monomeric plasticisers when the QuEChERS method is considered. In detail, mean recoveries appear good for DBS, ATBC, DEHA and ARMG with relative standard deviations $\leq$15 %.

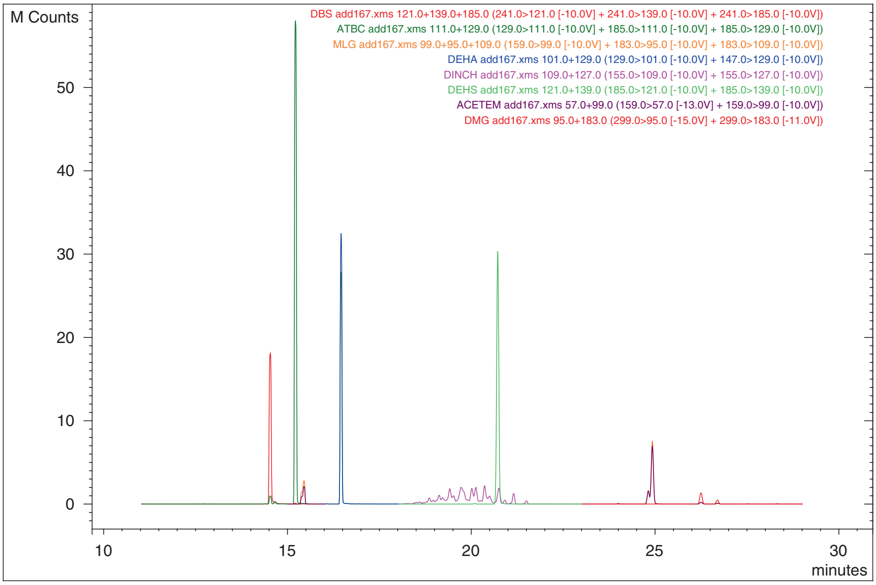

Fig. 3.11 Chromatograms of eight different monomeric plasticisers in oil samples, including DBS (*red line*), ATBC (*dark green line*), DEHA (*blue line*), DINCH (*purple line*), DEHS (*green line*) and DMG (*red line*, on the extreme right)

3.2.4 Analytical Method for ESBO in Foods

Almost all the methods used for the analytical determination of ESBO in foods derive from the method of Castle et al. [19], based on the determination in GC/MS of the methyl ester of diepoxylinoleic acid. This procedure requires the addition of one ester of the diepoxidised fatty acid as the internal standard, followed by the lipidic extraction of food samples and the transmethylation in alkaline conditions [19]. The lipidic extract is suitable for GC/MS analysis without further clean-up. Methylated epoxy fatty acids are then derivatised with cyclopentanone to form 1,3 dioxolanes which are successively determined by capillary GC/MS monitoring the single ions [19].

The Castle method has been used for a study concerning the content of ESBO in child foods [8]. In addition, it has been reported that lipid extraction and dioxolane derivatisation steps may be successfully avoided [20]. In fact, lipids may be transesterified in methyl esters directly into food samples with optimised reaction times, so that the water content does not disturb and avoids saponification [20]. Then, methyl esters of diepoxidised fatty acids are isolated through a normal phase in high-performance liquid chromatography (HPLC) before being transferred online to a GC/flame ionisation detector (FID) system. This method has been also modified by means of the elimination of LC preseparation using a polar column for GC (detector: MS), even if it is still possible to use FID in many cases [21].

A different procedure based on the use of a thermospray interface and reversed-phase liquid chromatography (RPLC) with a serial MS has been reported [22]. This method requires the extraction with dichloromethane of samples without further clean-up. The chromatographic separation is obtained through two C18 columns and mobile phase with the blend of acetic acid, acetone and acetonitrile in gradient conditions [22].

The procedure used at SSICA has been derived from Castle et al. [19], even if it has been noticeably modified in relation to the extraction step, as reported below.

In detail, food samples have to be considered in the following way:

(a) For foods with fat content from 0 to 5 %, the sample should be 30 g
(b) For products with fat content >5 %, the sampled food should allow the extraction of 1–1.5 g of lipids at least; the addition of water is needed in order to obtain 30 g of sample.

Subsequently, the addition of the solution of internal reference should be made in such a quantity that a concentration of 1 mg/g of fat in samples is obtained. Alternatively, 0.5 mg of solution of internal reference should be added when analysing a fat-free sample.

The introduction of a weighted sample in a beaker or in a container suitable for homogenisers is needed; next steps concern the following:

- The addition of 150 ml of hexane–acetone blend 50/50 for 10 min at 9,000 rpm
- The filtration on Buchner funnels with glass fibre filters
- The recovery of filtrates in a separating funnel and the separation between phases (aqueous phase can be eliminated)
- The collection of the organic phase in a flask containing 50 g of anhydrous sodium sulphate.

Subsequently, analysts have to:

(a) Go on with the filtration on a glass fibre filter washing sodium sulfate with portions of solution repeatedly
(b) Evaporate with the rotary evaporator and later under nitrogen, in order to eliminate any trace of solvent and only have the residual fat matter extracted from the sample.

Should the analysis be carried out on a food simulant, the following procedure has to be considered.

(a) Transfer 0.50 ± 0.02 g of D simulant (oil) or fat matter obtained through extraction (or the whole extract for non-fat samples) in a test tube. When speaking of oil simulant, add 0.5 ml of internal standard solution and evaporate the solvent under nitrogen
(b) Add 1 g of anhydrous sodium sulphate and 2 ml of methoxide sodium, shake and put in the stove at 65 °C for two hours shaking the test tube from time to time. After two hours, the extract in the test tube must be clear and homogeneous; should two phases are still observable, transmethylation would necessarily be repeated (the extract is not sufficiently dry)

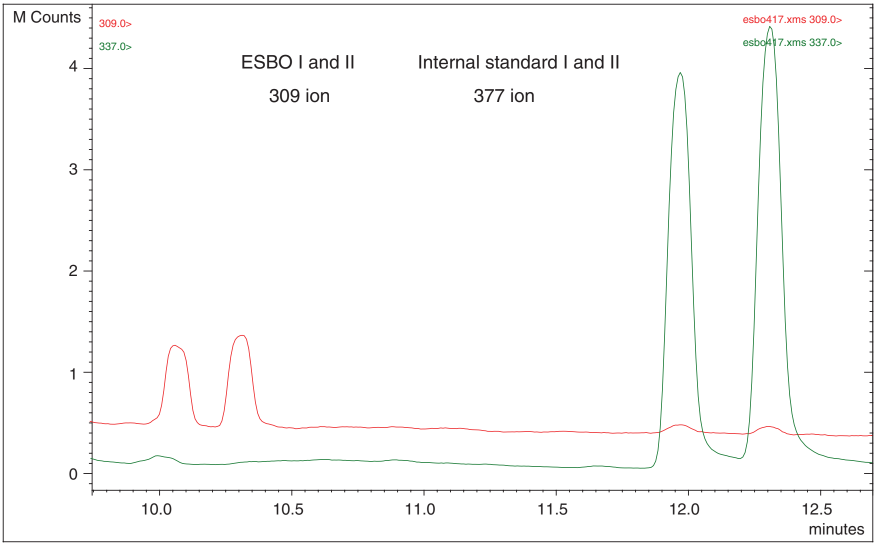

Fig. 3.12 Chromatograms of ESBO target ions (*red line*) and internal standard (*green line*) in olive oil

(c) Put the test tube under the stream of nitrogen and evaporate completely the solvent. Add in order: 2.5 ml of isooctane, 15 ml of cyclopentanone, 250 µl of boron trifluoride and immediately shake for 30 s. Add 5 ml of sodium chloride shaking again for 30 s

(d) Let stand to let separate phases and decant the supernatant liquid that will be possibly stored in freezer before being injected in the GC/MS apparatus, monitoring single ions. The standards for the calibration curve are added to oil simulant in order to have a behaviour similar to the sample; then, methylation and derivatisation are carried out like the sample. Figure 3.12 shows the chromatographic traces of ESBO target ions (309 m/z) at a concentration of 20 mg/kg and of the internal standard in oil (377 m/z).

With the above-described method, repeatability trials have been carried out on olive oil with the addition of 40 mg/kg of ESBO (10 tests) and on meat baby foods with the addition of 20 mg/kg of ESBO. Recoveries have been higher than 95 %; standard deviation values have been 6.7 and 8.9 % for olive oils and baby foods respectively.

3.2.5 Analysis of Polyadipates

The analytical determination of polyadipates is rather complex because of the lack of a single analytical reference substance.

A reliable method concerns [23] the determination of polyadipates through the extraction of foods with acetone/hexane 1:1 v/v, the subsequent transmethylation with etherated boron trifluoride/methanol, the clean-up procedure by size-exclusion chromatography and the final analysis of dimethyl adipate obtained by GC/MS.

The calibration has been performed submitting portions of polyadipate solution used as plasticiser in the food packaging, analysed with the same procedure of transmethylation and submitted to the clean-up used for the sample. This behaviour presumes that migrated polyadipates (small molecules) contain the same proportions of adipate present in the total polyadipate.

The analysis of polyadipates is carried out at the SSICA with the method suggested by Biedermann and Grob [24]. In addition, this procedure is based on the 'adipate' measurement unit. The food or simulating liquid is subject—after dissolution in tetrahydrofuran (THF)—to transesterification with sodium butoxide. Should polyadipate be present, it would be turned into dibutyl adipate: this molecule has a better chromatographic behaviour if compared with dimethyl adipate when obtained with another method [23].

The calibration is performed submitting portions of solution of dimethyl adipate, added of weighed quantities of plasticizer-free oil, to the same procedure of transesterification of the sample. A chromatogram of oil (D simulant) is shown in Fig. 3.13: the simulant has been put in contact with a PVC capsule plasticised with polyadipates.

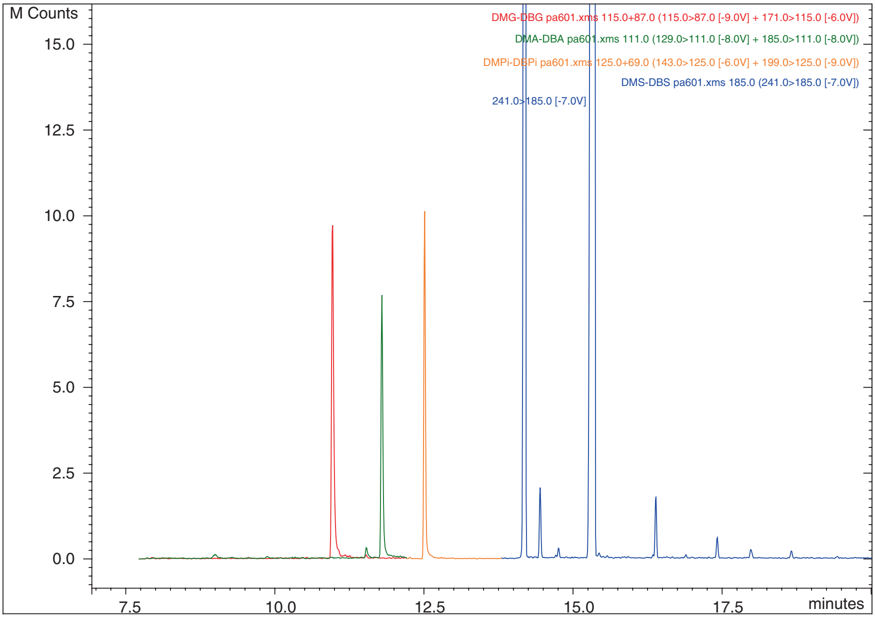

Fig. 3.13 Determination of polyadipates. GC/MS chromatogram of DMG (*red line*), DBA (*green line*), DBPi (*orange line*) and DBS (*blue line*) in oil

This procedure includes the use of internal standards: these substances are immediately added after sample weighing and before its dissolution in THF. Dimethyl pimelate (DMPi) is effectively used as an internal standard in the method of quantification of polyadipate plasticizer: the behaviour in the reaction of transesterification (times and percentage of reactions) is very similar to polyadipates [24].

Dimethyl glutarate (DMG) and dimethyl sebacate (DMS) are instead used as check standards. DMG has faster times of transesterification if compared with polyadipates and DMPi, while DMS has the slower times. However, 60 s of reaction should be sufficient for all involved substances [24]; therefore, DMG and DMS should be indicators of a good trend in the reaction.

At this stage, however, the obtained result (as dimethyl adipate) needs to be converted in polyadipate using a multiplying conversion factor. Probably, the calculation of this conversion factor is the most complex part of the analysis. As a consequence, polyadipate components (used as plasticiser in food packaging materials) with low molecular weights (MW) <1,000 Da must be preliminarily identified.

The chemical identification is carried out by GC/MS analysis of a solution of the polyadipate (if available) upon silylation reaction [25]. Because of the absence of polyadipate used as plasticiser, the original method [24] requires the solubilisation of a part of the packaging itself in THF.

After PVC precipitation (with methanol or ethanol) and the silylation reaction, the GC/MS analysis is carried out. The quantitative compositional analysis of low MW components is performed by means of a GC/FID apparatus with the same solution (as silylated polyadipate). Figure 3.14 shows GC/FID chromatograms of

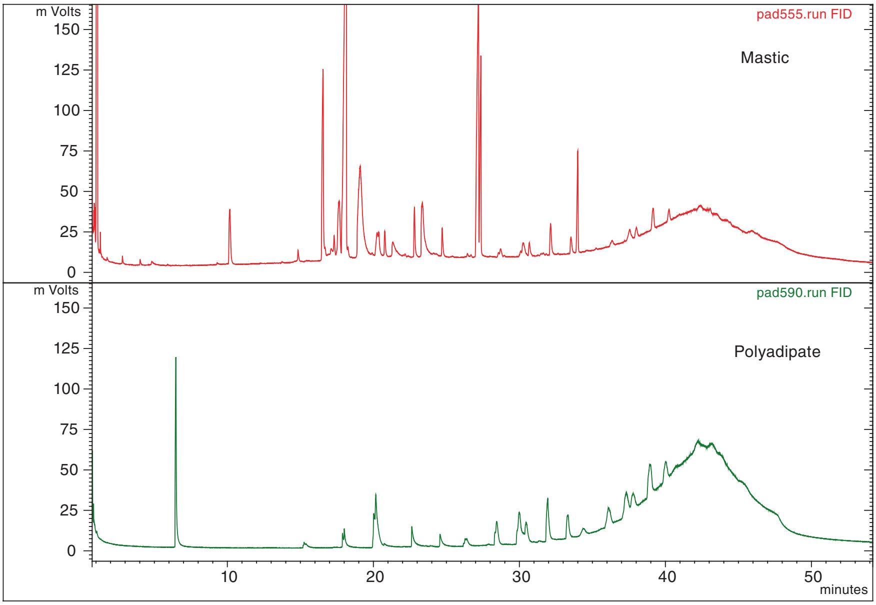

Fig. 3.14 GC/FID chromatograms of one pure polyadipate (*green line*) and the same obtained from the dissolution of mastic caps (*red line*)

a pure polyadipate and of the same set with other plasticisers obtained from the dissolution of mastic in capsules.

As a consequence, the useful conversion factor for the determination of polyadipates in food samples can be determined on the basis of GC/MS and GC/FID analyses [24]. The analysis of the profile obtained from pure polyadipate is certainly easier. At the same time, the profile obtained from the dissolution of plasticised PVC can give additional information concerning the presence of other plasticising substances.

3.3 Conclusions

PVC will probably be produced and still used for a long time, even if the criticism concerning the use of this material has taken place for several years. This problem concerns especially the production that involves highly toxic substances such as vinyl chloride and both waste disposal (production of dioxin during incineration, etc.).

The use of PVC for food packaging has not suffered further reductions (until now). However, several restrictions have already been taken and other limitation may be easily predicted in future, including the hypothesis of a replacement of PVC. Actually, dedicated studies on other materials and the evaluation of already existing materials for the replacement of PVC in food contact are being carried out. However, we can only try to use that material in the best way at the moment considering the knowledge and experience which have been gained so far.

Surveys and controls for packed food in glass jars and sealed with metal caps have been carried out by SSICA for several years [26, 27]. Research has mainly focused on oily foods or the contact of the capsules with the correct quantity of D simulant for these foods.

Results have shown that the traditional test based on regulations in force to evaluate new capsules before the contact with the food can hardly ever be representatives of what happens in the whole commercial life of the products. The development of a new specific test which could give a reliable forecast, before the contact, of migration before expiration and especially towards the end of the commercial life has failed. Probably, reasons for this situation are related to the remarkable diversification of food products and of heat treatments. Consequently, the type of product and the used technology can influence the commercial life of each product. It may be affirmed that the reproduction of standardised and short-lasting tests is difficult.

However, processes and analytical researches have definitely improved if compared to 10 years ago, when the first problems of specific migration in oily foods were tackled [28]. Nevertheless, it should be expected that the most efficient controls are carried out on packaged foods instead of simulating liquids. This approach implies obviously that related tests have to be carried out during the whole commercial life of food products. On these bases, the analytical reliability of obtained results—SML and global migration values up to the expiration date—can be confirmed [28]. A remarkable analytical work is clearly needed. On the other side, the above-mentioned approach appears the only reliable way for evaluating the trend and shelf life values of packaged foods from the viewpoint of chemical contamination.

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