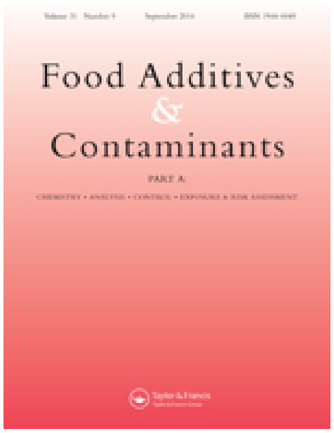

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Contamination of wines and spirits by phthalates: types of contaminants present, contamination sources and means of prevention

P. Chatonnet[a], S. Boutou[a] & A. Plana[a]
[a] Laboratoire Excell, Parc Innolin, 33700 Mérignac, France
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Contamination of wines and spirits by phthalates: types of contaminants present, contamination sources and means of prevention

P. Chatonnet*, S. Boutou and A. Plana

Laboratoire Excell, Parc Innolin, 33700 Mérignac, France

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This research determines the concentrations of various phthalates in French wines and grape spirits marketed in Europe or intended for export. Dibutyl phthalate (DBP), diethylhexyl phthalate (DEHP) and butyl benzyl phthalate (BBP) were the most frequently detected compounds in the wines analysed. While only 15% of the samples examined contained quantifiable concentrations (> 0.010 mg kg^{-1}) of DEHP and BBP, 59% of the wines contained significant quantities of DBP, with a median value as high as 0.0587 mg kg^{-1}. Only 17% of the samples did not contain any detectable quantity of at least one of the phthalates and 19% contained only non-quantifiable traces. In the spirits analysed, DBP (median = 0.105 mg kg^{-1}) and DEHP (median = 0.353 mg kg^{-1}) were the substances measured at the highest concentrations, as well as the most frequently detected (90% of samples). BBP was present in 40% of the samples at an average concentration of 0.026 mg kg^{-1}. Di-isobutyl phthalate (DiBP), which is not permitted in contact with food, was found in 25% of the spirits tested. According to the specific migration limits (SML) for materials in contact with food, slightly more than 11% of the wines analysed were non-compliant, as they exceeded the SML for DBP (0.3 mg kg^{-1}); just under 4% were close to the SML for DEHP. Concerning spirits, 19% of the samples analysed were considered non-compliant to the SML for DBP and nearly 7% were close to the SML for DEHP. The aged grape spirits analysed were often excessively contaminated with DiBP, which is not permitted to be used in contact with food (> 0.01 mg kg^{-1}). A study of various materials frequently present in wineries revealed that a relatively large number of polymers sometimes contained high concentrations of phthalates. However, the epoxy resin coatings used on vats represented the major source of contamination.

Keywords: phthalate; wine; spirit; food contact; DBP; DEHP

Introduction

Phthalate compounds are extremely widespread in our environment. These phthalic acid derivatives are commonly used as plasticisers in many plastics and a wide range of products may contain these types of materials (Bolgar et al. 2008; Piringer & Baner 2008). A number of phthalates have been used in a large number of industrial applications for over 50 years. These compounds are commonly found in plastics, synthetic coatings and paints to improve their flexibility, mechanical performance and resistance to temperature variations. Cosmetics are the second main application for phthalates. They improve the toughness of varnish and enhance adhesive qualities, or even the penetration of active ingredients. Thus, thousands of commonly used products may contain varying quantities of phthalates. Wine and grape spirits may, therefore, easily come into contact with materials likely to contain these substances. Due to their low solubility in water, phthalates migrate more easily into products with a high ethanol content. Spirits are, therefore, likely to contain higher concentrations than wines. However, wines may also be stored for long periods in contact with potentially contaminant materials and are subjected to a variety of handling and treatments where they may absorb phthalates to an extent that is still not clearly understood.

Phthalates are toxic to varying degrees depending on their chemical composition and their capacity to migrate within organisms. The toxicity of these compounds, particularly their carcinogenic potential, is still a controversial issue (Rivas et al. 1997; Blount et al. 2000; IARC 2000; Melnick 2001, 2002, 2003; Casajuana & Lacorte 2003). Nevertheless, some compounds are fairly unanimously considered to have major potential as endocrine disruptors (EPA 1997). The term "endocrine disruptors" is applicable to all xenobiotics with biomimetic properties. These substances do not present any significant acute toxicity. They are active at very low concentrations and may damage certain organic functions due to their chemical structure, which resembles certain natural hormones. Hormone receptors of living organisms are tricked by these compounds and induce inappropriate biological responses. As they act at very low concentrations and in synergy, standard toxicological thresholds are not really applicable to chemicals with these properties. Significant effects of phthalates have been detected in animals and certain results indicate that they may be responsible for congenital malformations of the male reproductive organs (xenoestrogen effect) (Duty et al. 2002). Exposure to *bis*(2-ethylhexyl)-phthalate (DEHP) causes modifications in the male reproductive system and the normal production of sperm

*Corresponding author. Email: pchatonnet@labexcell.com

in young animals (Blount et al. 2000). Exposure to DEHP and DINP has been associated with an increase in the occurrence of adenoma and hepatocellular carcinoma in rodents (IARC 2000; IRIS 2003). One of the proposed mechanisms to explain the phenomena observed in these animals is a proliferation of peroxisomes and cell organelles, a process not likely to be activated in primates or humans (IARC 2000). A number of researchers consider, however, that the carcinogenic potential of phthalates cannot be ignored (Vanden Heuvel 1999; Duty et al. 2002), but the IARC concluded that its original designation of DEHP as "possible carcinogenic to humans", which was based entirely on animal studies, should be changed to "cannot be classified as to its carcinogenicity in humans", in light of additional evidence on its mechanism of action (IARC 2000). Consequently, key concerns focus on their reproductive effects in humans, particularly fertility problems and the development of new-born babies.

The use of phthalates is regulated at an international level. European regulation No. 10/2011 EC of 14 January 2011 covers the use of phthalates in plastics likely come into contact with food and beverages. The regulation focuses specifically on certain phthalates, listed as toxic for reproduction in annex IV of regulation EU No. 143/2011 EC (CMR category 1B) and states that they will be completely banned, starting on 1 January 2015. The compounds concerned are: benzyl butyl phthalate (BBP), dibutyl phthalate (DBP) and diethylhexyl phthalate (DEHP). Changes in Danish regulations (BEK no. 1113 of the 26 November 2012) triggered a modification in French legislation in late 2012. Thus, French law No. 2012–1442 of 24 December 2012 now prohibits the phthalates cited above in implantable medical devices. Di-*n*-octyl phthalate (DNOP), di-*iso*-nonyl phthalate (DINP), and di-*iso*-decyl phthalate (DIDP) were already prohibited in childcare articles by Directive 2005/84 EC and order 2006-1361 of 9 November 2006.

There is currently no maximum permitted amount (MPA) in wine and spirits. Consequently, in the European Union specific migration limits (SMLs) are applicable for each chemical in the simulants corresponding to wines and spirits, i.e. the maximum quantity of a substance permitted in food (Regulation EEC 10/2011). A material intended to come into contact with food must not release a concentration likely to represent a health risk into the product consumed. For each type of material and foodstuff, a protocol for testing the phthalate migration must be implemented to guarantee its suitability for contact with food. The solutions simulating the behaviour of the food, the contact conditions (time and temperature), and analyses are, therefore, standardised (Regulation EEC 10/2011). The EC marking on coating and packaging materials does not guarantee their suitability for contact with food.

The interpretation of the results following certain holdups at the Chinese border in 2013 triggered a debate. However, the application criteria for the regulation were made more precise (Memo DGCCRF No. 2004-64 of 6 May 2004). The order dated 2 January 2003 and Article L.212.1 of the Consumer code concerning the general obligation of compliance specify that it is prohibited to market food that have been in contact with materials that are not compliant with the regulation on materials intended to come into contact with food. In this way, even if no MPA or tolerable daily intake (TDI) has yet been established for these compounds in wines and spirits, the maximum concentrations of these undesirable substances are still limited indirectly by the regulation on materials in contact.

Thus, a wine or spirit with a phthalate content above the SML imposed by the regulation on materials in contact with food would indicate that it had been in contact with a non-compliant material. The product intended for human consumption would thus also be non-compliant and unfit for sale in France and throughout the European Union. In view of the elements presented and the absence of published data on the subject, it was useful to analyse the phthalate concentrations in various types of French wines and spirits, as well as in several materials likely to be in frequent, prolonged contact with them, in order to identify the main sources of the contaminants found in these products. Following a rapid overview of the contamination status of wines and spirits in France, we present a few results identifying the major contamination sources in the wine-making industry, as well as solutions for eliminating them.

Material and methods

The various phthalates (Figure 1) were assayed in liquids by GC-MS (Agilent Technologies, 7890A; Les Ulis, France; http://www.chem.agilent.com) in electron impact mode with detection in SIM mode (70 eV, source temperature: 250°C, transfer line: 300°C, quadrupole: 150°C, Agilent Technologies, MSD 5975), according to the OIV SCMA 477-2013 protocol for wine and OIV SCMA 521-2013 for spirits (OIV 2013a, 2013b) with standard calibration (0–1 mg l^{-1}) and deuterated internal standards (Restek, Lisses, France; http://www.restek.fr). The phthalates were extracted from the liquid matrix using isohexane ≥ 95% for wine and toluene ≥ 99.5% for spirit (Aldrich, Saint-Quentin Fallavier, France; http://www.aldrich-sigma.fr) and 1 µl injected with a 10 µl syringe with the MPS2 sampler (Gerstel, Mülhein an der Ruhr, Germany; http://www.gerstel.com) and the assays compared with deuterated standards for each compound (Restek) after separation on a non-polar column DB5-MS 30 m × 0.25 mm, phase thickness: 0.25 µm (Agilent technologies), 1 ml min^{-1} helium, temperature: 100°C for 1 min, programmed up to 270°C at 10°C min^{-1}, held for 2 min, then up to 300°C at 25°C min^{-1}, and held for 8 min. The substances were detectable (LOD) under these conditions between 0.004 (DMP, DEP, DiBP,

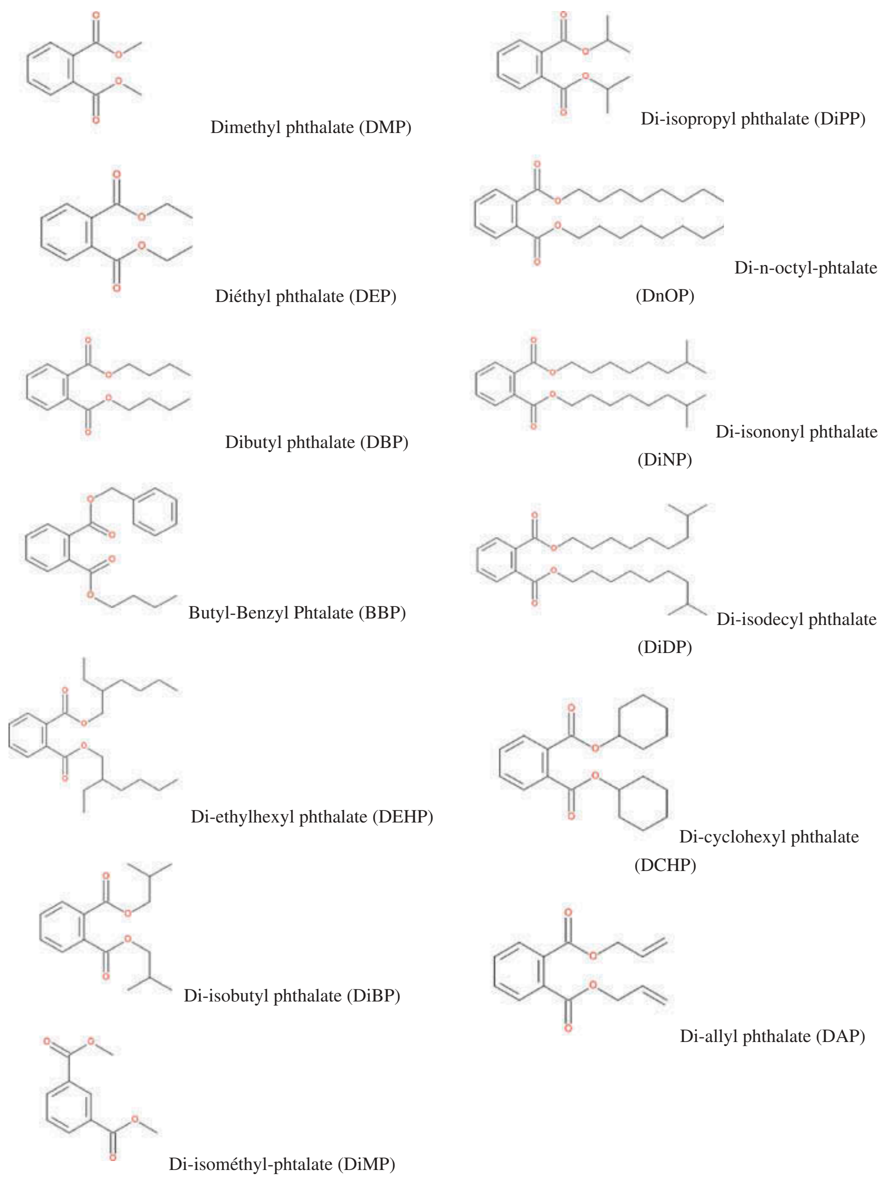

Figure 1. Chemical structure of phthalates.

DnBP, BBP, DCHP, DEHP and DnOP) and 0.020 (DINP and DIDP) mg l^{-1} and quantifiable (LOQ) at 0.01 (DMP, DEP, DiBP, DnBP, BBP, DCHP, DEHP and DnOP) and 0.05 (DINP and DIDP) mg l^{-1} (coefficient of variation for repeatability: 6%, for reproducibility: 8% determined at 0.04 and 0.08 mg l^{-1}). Blank test are performed for each assay (typical level in the blank are below 0.001 mg l^{-1}).

The dry materials in contact with wines and spirits were analysed using the protocol developed by the Guangzhou Inspection and Quarantine Technology Center (Huang et al. 2011) (Soxhlet extraction by dichloromethane, GC-MS quantification by isotope dilution), found to be more effective than the European EN 14372:2004 and American ASTM D7083-04 methods. The coefficient of variation for repeatability varied from 3% to 7% (range = 0.1–150 g kg^{-1}), depending on the compound, with a recovery rate from 98% to 99.9% for the phthalates targeted; the detection threshold was 1 µg g^{-1} and the quantification threshold 5 µg g^{-1}. To simplify the expression of results in the various matrixes, all the results in liquid solution are expressed in mg kg^{-1} to take into account the variation of volumic masses with the alcoholic grade. Alcoholic content was determined by infrared spectrometry (Dubernet & Dubernet 2000).

Migration test under model conditions

Glass plates, 50 × 100 mm, impregnated with epoxy resin applied according to the manufacturer's technical recommendations, were exposed with a 6 dm^2 kg^{-1} surface in contact to a solution simulating wine (20% v/v ethanol, 3% acetic acid) maintained at 60°C ± 0.5 for a variable period (10–60 days). Plastic materials from hoses used for pumping were analysed under the same conditions. The method used was compliant with EC Regulation 10/2011.

Results

It was not possible to conduct a statistically representative study that would produce accurate conclusions. However, the number of samples analysed (n = 100) and the geographical diversity of the market-ready French products analysed provided an excellent overview of the presence of phthalates in wine. The smaller number of samples (n = 30) and more limited range of spirits (from south-west France) somewhat restricted the scope of the results.

Types and concentrations of phthalates assayed in the wines

Significant quantities of only three out of 13 target compounds were found: dibutyl phthalate (DBP), diethylhexyl phthalate (DEHP) and butyl benzyl phthalate (BBP). The other molecules were not present at detectable levels. The concentrations measured varied considerably from one sample to another (Table 1), indicating significant variations in exposure to contaminant sources. While only 15% of the samples analysed contained quantifiable concentrations (> 0.010 mg kg^{-1}) of DEHP and BBP, 59% of the wines contained significant quantities of DBP, with a median value as high as 0.0587 mg kg^{-1}. Only 17% of the samples did not contain any detectable quantity of at least one of the phthalates targeted by regulation EU No. 143/2011 EC and 19% contained only non-quantifiable traces. Di-isobutyl phthalate (DiBP) was only detected in trace amounts (between 0.01 and 0.004 mg kg^{-1}) in 4% of the samples.

Types and concentrations of phthalates assayed in grape spirits

Due to their higher ethanol content and the solubility characteristics of phthalates, spirits were likely to contain larger amounts of these compounds. In practice, the market-ready spirits analysed, containing between 40% and 45% v/v alcohol, had slightly higher concentrations (Table 2) but the main differences concerned the type and frequency of measurable levels. DBP (median = 0.105 mg kg^{-1}) and DEHP (median = 0.353 mg kg^{-1}) were measured in the highest concentrations and with the greatest frequency (90% of samples). BBP was detected in 40% of the samples (compared with 15% of the wines), with an average concentration of 0.026 mg kg^{-1} but considerable variability.

Di-isobutyl phthalate (DiBP) was detected in 25% of the spirits analysed. However, only the oldest spirits (over 20 years of age) in our survey contained measurable concentrations (Figure 2). Only traces of this compound were detected in the remaining samples (< 0.010 mg l^{-1}, in 10% of samples). This particular phthalate seems, therefore, only to have contaminated spirits produced during a certain period, as it was not detected in the younger samples. Finally, 100% of the spirits analysed contained at least one of the phthalates targeted by European Union Regulation No. 143/2011 EC.

Phthalate concentrations in various materials that come into contact with wines and spirits

Several materials frequently used in winery fermentation and ageing facilities and polymer compounds likely to contain phthalates were analysed in order to identify the major source(s) of contamination in wines and spirits. In wineries, various polymer-based items are used for pumping, storing, and handling wines and spirits (vats, pumps, hoses, gaskets, tanks, recipients, epoxy-resin-based

Table 1. Concentration of the most frequent phthalates in wines (n = 100).

Molecule (mg kg^{-1})	Average	Standard deviation	Coeficient of variation	Median	Minimum	Maximum	% of wine samples with phtalates > LOQ
DBP	0.273	0.591	217%	0.0587	<0.004	2.212	59%
BBP	0.008	0.024	314%	0.00	<0.004	0.122	15%
DEHP	0.134	0.350	262%	0.00	<0.004	1.1317	15%

Table 2. Concentration of the most frequent phthalates in wine spirits (n = 30).

Phthalate (mg kg^{-1})	Average	Standard deviation	Coefficient of variation (%)	Median	Minimum	Maximum	Percentage of spirit sample with phatalates > LOQ
DBP	0.314	0.323	103	0.104	< 0.004	1.083	90
BBP	0.026	0.037	142	0.000	< 0.004	0.096	40
DEHP	0.513	0.326	64	0.353	< 0.004	1.522	90
DiBP	0.103	0.046	45	0.000	< 0.010	0.170	25[a]

Note: [a]Samples of more than 20 years old, cf. Figure 2.

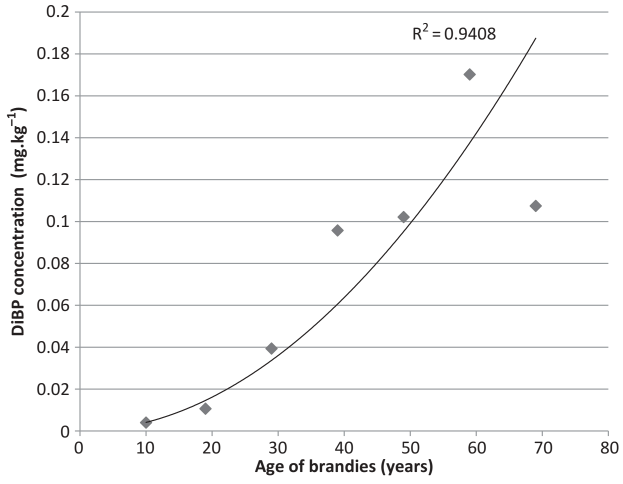

Figure 2. Relationship between the DiBP content of wine spirits from the same origin (Armagnac) and their ageing.

coatings, etc.), remaining in direct contact with the liquids for variable periods of time (Table 3). Several phthalates are included on the positive list of molecules permitted in materials in contact with food. However, DMP, which is not permitted, was also identified in the wall of a polyester-resin and glass-fibre vat.

Generally, polyethylene- (HDPE and LDPE) and polysiloxane-based (silicones) materials contained traces, at most, of phthalates. The hoses used for pumping contained high concentrations of DEHP or DiNP, depending on their composition. Some types of epoxy resins used in coatings on storage and fermentation vats may represent a major source of contamination by DBP and DiBP.

Some of the corks used in wine and spirits bottles consist of plastics and others of cork agglomerated with various synthetic materials. Analysis of several of these materials did not identify any significant sources of contamination (Table 4). However, the presence of small quantities of DiBP was noted in certain synthetic corks, whereas it should not be present at all in a material intended for contact with beverages.

Analysis of a few plastic bags used to package wines for sale ((A) 2.5 and (B) 5 L bag in box, BIB) revealed (Table 5) that wine bag B parts may contain DiNP. However, in view of the mass and surface area of this type of container in contact with wine and the SML for DiNP, the risk of problematic migration may be considered non-existent. The bags themselves, which sometimes remain in direct contact with the wine for long periods, only contained traces of phthalates without any significant consequences.

Identifying the risk of contamination by materials in direct contact

All materials that come into contact with food must have food contact certification, issued on the basis of the overall migration of substances from the material into the target foodstuff (or, more exactly, the standardised simulant). The migrated substances must not affect the organoleptic quality or composition of the foodstuff considered. The producer must be able to prove compliance with legislation and, for example, in the case of a specific plastic, issue a document of compliance (DoC) based on the necessary analytical work, calculations and considerations (EC Regulation 10/2011). Good manufacturing practices must ensure that migration does not exceed 10 mg dm^{-2}, the limit used to certify that a plastic-based material is inert on a legal point of view in case of no SML.

If a particular substance in the composition of the material represents a toxicological risk, as is the case of phthalates, it is also necessary to determine whether it complies with the SMLs, measured under standardised conditions. These SML vary according to the compounds and foodstuff concerned. Table 6 presents a summary of the main phthalates authorised for contact with wines and spirits; no unauthorised substances must be detectable (< 0.01 mg kg^{-1} SML), measured under standardised conditions. SMLs vary according to the compounds and food concerned (Table 6).

In fact, the phthalate content of a material does not give any indication of the actual risk of migration into wines and spirits. The migration potential may vary considerably, depending on the type, structure and texture of the material, the molecules considered and the surface exposed to contact with the beverages. It is, therefore, necessary to conduct migration tests under standardised conditions (simulant: 20% v/v ethanol for wine and 50% v/v for spirits, 3% acetic acid, 10 days at 60°C) to determine the risk that a given material represents a significant source of contamination.

Thus, the three pump hoses analysed by total extraction contained highly variable concentrations of phthalates (Table 3, corrugated hoses 3–5). However, when the concentration of each molecule was measured under standardised simulation conditions, the three materials were found to be compliant with legislation (Table 7). Nevertheless, it is quite clear that, at equivalent performance and cost, it is preferable to avoid any risk by using materials that do not contain any phthalates, measured by total extraction. The two types of measurements are, therefore, complementary.

What is the value of food contact certification provided by the manufacturer? Very little, if the SML have not been determined, especially if the alcohol content of the simulant is not representative of the product stored – epoxy resins are widely used in contact with spirits although they have not been tested above 20% v/v ethanol. The example below concerns two wines with the same alcohol content (12.5% v/v ±0.1), stored in the same vats coated with an epoxy resin reputed to be food contact certified, applied in 1995 (18 years earlier), for periods varying from 18 months to 2 years (Table 8).

Table 3. Phthalate content in different material frequently in contact with wines or spirits in the wineries.

	Concentration in μg.g^{-1} of dry material, total extraction Soxhlet-dichloromethane																
Molecules	Rotor of rotative pump	Tank seal	Stator of pump moneau	Peristaltic pum tube	Glass fibre tanks	Plastic tank	Plastic hose 1	Plastic hose 2	Plastic hose 3	Plastic hose 4	Plastic hose 5	Plastic basket	Plastic bin 1	Plastic bin 2	Sulphurous solution can	Epoxy coating 1	Epoxy coating 2
DMP	n.d.	n.d.	n.d.	n.d.	**4237**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DCHP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Traces	Traces
DAP	n.d.	n.d.	n.d.	n.d.	Traces	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DBP	n.d.	Traces	Traces	Traces	n.d.	n.d.	Traces	Traces	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Traces	**82,419**
DiBP	Traces	Traces	**28**	**72**	Traces	Traces	**46**	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	n.d.	**2783**
DiPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BBP	n.d.	n.d.	n.d.	**24**	n.d.	n.d.	**37**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEHP	**848**	**29,684**	Traces	Traces	**30**	Traces	**15,876**	**199,705**	33	Traces	268	**41**	Traces	**97**	Traces	n.d.	40
DOP	n.d.	**50**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**65,263**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiNP	Traces	**225**	n.d.	n.d.	n.d.	n.d.	Traces	**113**	n.d.	n.d.	**102,081**	n.d.	n.d.	Traces	n.d.	n.d.	n.d.
DiDP	n.d.	**1802**	n.d.	n.d.	n.d.	n.d.	**58**	**2037**	**3249**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Note: Bold values indicate quantifiable values.

Table 4. Phthalates content of different kind of stoppers used for wines or spirits.

Phthalates	Concentration (μg per cork), total extraction Soxhlet-dichloromethane												
	Stopper Nomacorc Light 1	Stopper Nomacorc Light 2	Stopper Nomarcorc Cclassic 1	Stopper Nomacorc Classic 2	Stopper Nomarcorc Classic 3	Stopper Vineo A	Stopper VINEO C	Red plastic seal	Saranex liner from screw cap	PET liner from screw cap	Micro-granulated cork DIAM3	Micro-granulated cork DIAM5	Micro-granulated cork Mytik
DMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DCHP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Traces	Traces	n.d.	n.d.	n.d.
DAP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DBP	n.d.	Traces	Traces	Traces	Traces	Traces	n.d.	n.d.	Traces	n.d.	Traces	n.d.	n.d.
DiBP	305	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	n.d.	Traces	n.d.	n.d.
DiPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BBP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEHP	Traces	234	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	156	n.d.	Traces
DOP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiNP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Traces	n.d.	n.d.
DiDP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 5. Phthalates content of different element of wine bags (Bag in Box™ style).

Phthalates	Concentration (µg g^{-1}), total extraction Soxhlet dichloromethane					
	Wine bag BIB (A)	Neck BIB (A)	Faucet BIB (A)	Wine bag BIB (B)	Neck BIB (B)	Faucet (B)
DMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiMP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DCHP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEP	Traces	n.d.	n.d.	n.d.	n.d.	n.d.
DAP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DBP	n.d.	n.d.	n.d.	Traces	n.d.	n.d.
DiBP	n.d.	Traces	Traces	Traces	Traces	Traces
DiPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BBP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEHP	Traces	48	Traces	Traces	Traces	Traces
DOP	n.d.	n.d.	n.d.	828	n.d.	n.d.
DiNP	n.d.	n.d.	n.d.	21,803	n.d.	n.d.
DiDP	n.d.	34	n.d.	n.d.	n.d.	n.d.

Table 6. Specific migration limit (SML) of different phthalates in alcoholised products following CE/10/2011.

Phthalates	Abbreviation	SML mg kg^{-1}
Benzyl-butyl phthalate	BBP	30.0
Di-ethyl phthalate	DEP	Not allowed (< 0.01)
Di-butyl phthalate	DBP	0.3
Di-methyl phthalate	DMP	Not allowed (< 0.01)
Di-methyl-*iso* phthalate	iDMP	Not allowed (< 0.01)
Di-ethylhexyl phthalate	DEHP	1.5
D-*n*-octyl phthalate	DNOP	60.0
Di-*iso*-nonyl phthalate	DINP	∑ DiNP + DiDP
Di-*iso*-decyl phthalate	DIDP	< 9.0
Di-allyl-phthalate	DAP	Not allowed (< 0.01)
Di-*iso*-pentyl phthalate	DiPP	Not allowed (< 0.01)
Di-*iso*-butyl-phthalate	DiBP	Not allowed (< 0.01)
Di-cyclohexyl phatalate	DCHP	Not allowed (< 0.01)

Analysis of the first wine detected DBP, which is authorised for contact with food, but at a concentration exceeding the SML. A small quantity of DiBP, not permitted in contact with food, was also detected in the same wine at a level in the vicinity of the SML. Consequently, this wine had been kept in contact with a material that did not comply with the current regulation on materials in contact with food and could not, therefore, be marketed for human consumption. The other wine was stored in the same vats for a shorter time (19 months compared with 25 months); the migration rate was not only directly proportional to storage time. This wine was compliant with the regulation as the concentrations measured were lower than the SML. If the wine had been stored in the same vat for a longer period, it would probably no longer have been compliant. Indeed, analysis of the coating revealed high concentrations of DBP (0.08%), as well as smaller, but nevertheless significant, quantities of DiBP (0.002%), although it is prohibited for items in contact with food. In view of the phthalate content of the coating and the annual migration rate (measured in this case at between 0.005 and 0.015% per year), this type of epoxy resin may be considered to have almost infinite potential for contamination.

Overall, comparing the concentrations measured in our sample of wines and spirits and comparing them to the SML for materials in contact with food, slightly over 11% of the wines analysed were non-compliant, as they exceeded the SML for DBP (0.3 mg.kg^{-1}), and just under 4% were close to the SML for DEHP. Concerning spirits, 19% of the samples analysed were considered non-compliant, as they exceeded the SML for DBP, and nearly 7% were close to the SML for DEHP. The aged spirits analysed were frequently excessively contaminated with DiBP, which is not permitted for items in contact with food (> 0.01 mg kg^{-1}). Products that come into contact with a material that fails to comply with the regulation on materials in contact with food should not be sold.

A solution for preventing contamination by non-compliant epoxy resins coating tanks

Some vats coated over 10 years ago have a high potential for contamination. It is advisable to stop using these containers for prolonged storage or envisage renovating them with modern resins that comply with the current regulation, or, better still, products that do not contain any phthalates or bisphenol-A and its derivatives, in anticipation of upcoming changes in food-contact regulations around the world. The latter option is, of course, the best but also the most expensive.

To overcome this disadvantage, we devised a specific preparatory treatment to improve adhesion (not presented in this article), so that a new coating without any undesirable substances can be applied as a barrier layer, to

Table 7. Evaluation of the conformity of different plastic hoses used for the manipulation of wines and spirits in accordance with European regulation of the materials in contact with foods.

Trial parameters	Plastic hose 1	Plastic hose 2	Plastic hose 3	
Mass (g)	60.341	46.981	41.517	
Height (dm)	0.52	0.53	0.6	
External radius (dm)	0.52	0.5	0.5	
Internal radius (dm)	0.44	0.4	0.42	
Total area (dm^2)	3.52	3.56	3.92	
	µg dm^{-2}			
DMP	n.d.	n.d.	n.d.	
DiMP	n.d.	n.d.	n.d.	
DCHP	n.d.	n.d.	n.d.	
DEP	Traces	Traces	Traces	
DAP	n.d.	n.d.	n.d.	
DBP	n.d.	n.d.	n.d.	
DiBP	n.d.	n.d.	n.d.	
DiPP	n.d.	n.d.	n.d.	
BBP	n.d.	n.d.	n.d.	
DEHP	n.d.	n.d.	n.d.	
DOP	n.d.	**180.3**	n.d.	
DiNP	n.d.	n.d.	**71.9**	
DiDP	Traces	n.d.	n.d.	
	Potentiel of migration in µg L^{-1}			**SML µg L^{-1}**
DMP	n.d.	n.d.	n.d.	<0.001
DiMP	n.d.	n.d.	n.d.	<0.001
DCHP	n.d.	n.d.	n.d.	<0.001
DEP	Traces	Traces	Traces	<0.001
DAP	n.d.	n.d.	n.d.	<0.001
DBP	n.d.	n.d.	n.d.	3260
DiBP	n.d.	n.d.	n.d.	<0.001
DiPP	n.d.	n.d.	n.d.	<0.001
BBP	n.d.	n.d.	n.d.	3260
DEHP	n.d.	n.d.	n.d.	1630
DOP	n.d.	**2968.1**	n.d.	6520
DiNP	n.d.	n.d.	**1437.5**	6520
DiDP	Traces	n.d.	n.d.	6520
Conclusion*	**Conform**	**Conform**	**Conform**	

Note: *From CEE N°10/2011 and law RF N° 2012–1442 with a volumetric mass of the solution of 920 g L^{-1}. Bold values indicate quantifiable values.

prevent the migration of contaminants from the underlying layer without removing the old coating. Tests were carried out on experimental plates prepared in the laboratory (*x* cm) kept in contact with a model, alcohol-based solution (20% v/v ethanol, 3% acetic acid, x dm^2 l^{-1}), at 40°C ± 0.5, for variable periods (10–60 days), with three repetitions per test, in accordance with the standard protocol. Barrier layer (A) or (B) (coating composition and density not disclosed) was applied on top of an epoxy-based coating containing 10 mg g^{-1} DBP and DiNP and phthalate migration was measured over time (Figure 3).

Despite a significant DiNP content in the control layer, it did not migrate into the model solution in significant concentrations (SML DiNP = 9 mg kg^{-1}). In contrast, DBP, present at the same concentration, migrated into the solution much more easily and quite rapidly, frequently exceeding the SML (0.3 mg kg^{-1}). When coating (A) was applied, migration was reduced by 71% compared with the control after the standard experimental period of 40 days but the values still exceeded the SML for DBP (2.3 mg kg^{-1}). A detailed examination of the outer coating revealed cracking through the barrier layer, indicating a lack of homogeneity and integrity of the protective coating after its interaction with the alcohol and/or acid of the simulant. In contrast, coating (B) effectively prevented the migration of DBP from the contaminated coating 100% effectively, despite the tough physicochemical conditions, and migration levels remained systematically below the SML. Coating (B) showed good mechanical resistance to the environment and provided an effective barrier layer.

The use of a solution of this type would provide a remedy for non-compliance due to old resin coatings without the slow, expensive process of completely removing and replacing contaminant coatings. This test needs to be repeated using a spirit with an alcohol content much higher than 20% to confirm the solution's effectiveness in that specific case.

Discussion and conclusions

This research showed that DBP, DEHP, and BBP were the main phthalates found in wines and spirits. Statistically speaking, DBP is the most common, abundant migrant found in wine, while DBP and DEHP are the two most common, abundant phthalates in spirits. Although DiBP is not on the positive list of phthalates authorised for contact with food, measurable concentrations are occasionally detected in spirits over 20 years old and only rarely in wine.

The DBP content of approximately 11% of the wines and 19% of the spirits analysed exceeded the authorised SML for alcoholic beverages, as specified in regulation No. 10/2011 EC of 14 January 2011 on materials intended to come into contact with food. Consequently, according to the order dated 2 January 2003 and Article L.212.1 of the Consumer Code, these products are non-compliant and should not be sold for human consumption.

Analysis of the various materials frequently present in wineries revealed that quite a large number of polymers, sometimes containing large quantities of phthalates authorised for contact with food, could easily come into contact with wines and spirits. It is advisable to eliminate all materials containing these types of compounds from wineries. However, in view of the migration parameters of phthalates, epoxy coatings used in vats represent the major source of contamination in wines and spirits. Certain phthalates not permitted for contact with food, such as DMP and diBP, were also identified in the walls of polyester-and-glass-fibre vats and in some epoxy resins. It is, therefore, advisable for producers to analyse the coatings used in their vats, especially

Table 8. Phthalate contents of two wines stored in the same tank coated with an epoxy resins during different times.

	Wine 1	Wine 2	
Storage duration (months)	25	19	SML (mg kg^{-1})
Wine			
DBP mg kg^{-1}	0.453	0.158	0.300
DiBP mg kg^{-1}	0.012	n.d.	0.010
Conformity of wine vs SML of material	No	Yes	
Epoxy coating of the tank			
DBP	80	mg g^{-1}	
DiBP	2	mg g^{-1}	
Density of the coating	135	g m^{-2}	
Ratio area/volume of the tank	0.066	m^2 L^{-1}	
Coating mass/wine volume one level coating	8.97	g L^{-1}	

if they were applied over 10 years ago, to obtain a clear assessment of the contamination risks on their premises.

If the coating is contaminated, the vats concerned should no longer be used or the time the wine is kept in them should be reduced considerably. As spirits have higher ethanol content, they always extract phthalates trapped in materials more rapidly and extensively than wines. Contaminated coatings should be eliminated and the vats renovated with modern resins that do not contain undesirable phthalates. Our laboratory tests also led to the development of an alternative technique that should make it possible to leave contaminated coatings in place by applying a barrier layer, which costs less and is a lot less time-consuming. The presence of other substances frequently associated with phthalates (bisphenol-A and derivatives, nonylphenol, aromatic amines, maleic acid and derivatives, and 1.3-butadiene), also likely to exceed regulatory limits, should also be investigated.

In view of the major and secondary contamination sources identified in this research, it appears to be possible to achieve a rapid reduction in contamination risk levels and non-compliance within a short time. It is advisable that producers conduct a risk assessment on a case-by-case basis as soon as possible. The elimination of all materials containing significant quantities of phthalates from wine-making premises is advisable and possible in the short-term.

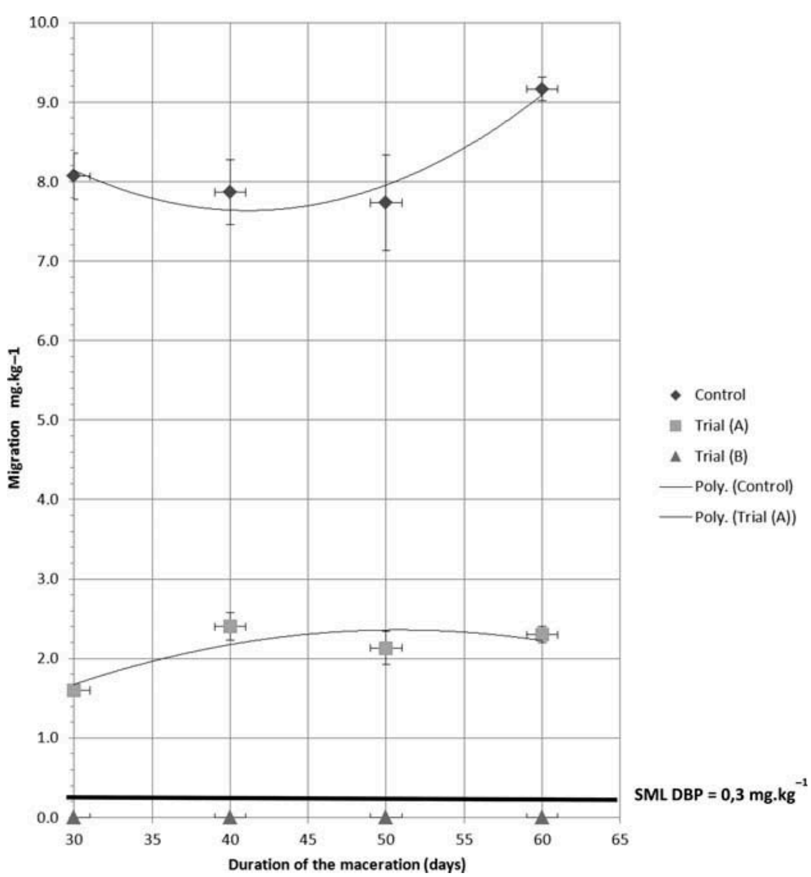

Figure 3. Study of the barrier effect of different epoxy coatings to reduce phthalate migration – evolution of the DBP migration versus time in a model solution simulating wine comportment (three repetitions).

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