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Title: Study of the repartition of phthalate esters during distillation of wine for spirit production

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Keywords: Phthalate Esters; Dispersive Liquid-Liquid Micro-Extraction; Gas Chromatography-Mass Spectrometry; Distillation; Distilled Alcoholic beverages.

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Abstract: Due to health concerns and legal matters, an investigation to limit phthalates esters (PEAs) in spirits is necessary. A lab still was used to perform pilot distillations according to the official method for brandy production in order to explore the repartition into the distilled fractions of each PAE. The process was divided in two steps: a première chauffe and a bonne chauffe. The former step included the cut into heads, heart and tails, while the latter into heads, brandy, secondes, and tails. The behaviour of each PAE during distillation was affected by its own chemical nature. Dibutyl phthalate (DBP) was entirely carried over into the distillate, while bis(2-ethylhexyl) phthalate (DEHP) only partially, and diisononyl phthalate (DINP) accumulated in the stillage. During the bonne chauffe, DBP and DEHP accumulated in the secondes more than in the brandy. A rectification step of the secondes was demonstrated to considerably reduce PAEs concentration.

Centro per il Miglioramento e la Valorizzazione delle Risorse Biologiche Agroalimentari - BIOGEST-SITEIA

Centro Interdipartimentale per il Miglioramento e la Valorizzazione delle Risorse Biologiche Agro-Alimentari
Piazzale Europa, 1 - 42124 Reggio Emilia (Italia)

May 4th, 2017

Dear Editor,

I am sending you a copy of the revised Ms. entitled: "Study of the repartition of phthalate esters during distillation of wine for spirit production".

All reviewers' comments were carefully considered and accepted in large part.

Short title: Repartition of phthalates during distillation for spirit production

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Best regards,
Giuseppe Montevecchi

Response to reviewers' comments:

Reviewer #1: The work "Study of the repartition of phthalate esters during distillation of wine for spirits production" overall is good science. My opinion is that it can be considered for publication in Food Chemistry, after a revision of English.

The authors recommend taking into account the recent publication:

1) Extraction and GC-MS analysis of phthalate esters in food matrices: a review. MV Russo, Avino P, L Perugini, I Notardonato. RSC Advances 5 (46), 37023-37043 (2015)

The English was accurately revised. We included the suggested reference in the text.

Reviewer #2: PAEs are used as surfactants, emulsifying agents, stabilizers, dispersants, and lubricants. As a consequence of their diffusion, PAEs become process contaminants for food. These substances are cause of great concern as endocrine disrupting chemicals, mainly related to human reproduction. Though, the content of PAEs in the samples was influenced by the level of PAEs contamination in the raw material and by the effect of the concentration that occurred during ageing, the repartition into heads, heart, and tails of each PAE during distillation of the base wine is unknown. This paper studied for that in order to provide a tool to improve brandy purification. The work was well-done. I recommend it to be accepted after minor revision.

1. HPLC chromatogram and GC/MS chromatogram should be given.

HPLC chromatogram has just one peak at 24 min (line 185), while GC/MS chromatogram is now provided as a figure and more details about peaks identification and quantification are now included (lines 171-175).

2. The language needs polish and the table should be changed as three-line table.

English was accurately revised and Table 2 was converted into a three-line table.

EDITORIAL COMMENTS

Abstract: Put all sentences into a single paragraph.

Done.

Line 23-24: Provide DBP, DEHP and DINP in full rather than abbreviations.

Done.

Line 75: are the concentrations given for DBP, DEHP and DINP acceptable limits? Indicate what these numbers refer to.

The values (now line 77) are the maximum concentrations imposed for each substance by the Chinese law. The sentence was rewritten to explain it in a clearer way.

Table 2: Do not use more than two significant digits in the uncertainty value and match the level of precision in the number, e.g. 19.4 ± 1.3 rather than 19.440 ± 1.330; 2.7 ± 0.2 rather than 2.694 ± 0.167 etc.

Done.

***Highlights (for review)**

Study of the repartition of phthalate esters during distillation of wine for spirit production

Giuseppe Montevecchi, Francesca Masino, Nicolas Di Pascale, Giuseppe Vasile Simone, Andrea Antonelli

Highlights: > It is necessary to limit contaminants such as phthalates esters (PAEs) > The behaviour of PAEs during distillation was investigated using a lab still > DBP and DEHP were carried over into the distillate, DINP accumulated in the stillage > Rectification of the secondes is effective to considerably reduce PAEs concentration

Study of the repartition of phthalate esters during distillation of wine for spirit production

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Abstract

Due to health concerns and legal matters, an investigation to limit phthalates esters (PEAs) in spirits is necessary. A lab still was used to perform pilot distillations according to the official method for brandy production in order to explore the repartition into the distilled fractions of each PAE. The process was divided in two steps: a *première chauffe* and a *bonne chauffe*. The former step included the cut into heads, heart and tails, while the latter into heads, brandy, secondes, and tails. The behaviour of each PAE during distillation was affected by its own chemical nature. Dibutyl phthalate (DBP) was entirely carried over into the distillate, while bis(2-ethylhexyl) phthalate (DEHP) only partially, and diisononyl phthalate (DINP) accumulated in the stillage. During the *bonne chauffe*, DBP and DEHP accumulated in the secondes more than in the brandy. A rectification step of the secondes was demonstrated to considerably reduce PAEs concentration.

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Keywords: Phthalate Esters; Dispersive Liquid-Liquid Micro-Extraction; Gas Chromatography-Mass Spectrometry; Distillation; Distilled Alcoholic beverages.

Chemical compounds studied in this article:

Dibutyl phthalate, DBP (PubChem CID: 3026)

Bis(2-ethylhexyl) phthalate, DEHP (PubChem CID: 8343)

Diisononyl phthalate, DINP (PubChem CID: 590836)

Benzyl butyl phthalate, BBP (PubChem CID: 2347)

1. Introduction

Phthalate esters (dialkyl or alkylarylesters of 1,2-benzenedicarboxylic acid, also known as PAEs) are a family of chemicals abundantly used since 1930 for a wide spectrum of different industrial applications. PAEs are chemically produced by the reaction of phthalic anhydride with straight-chain or branched alcohols. Therefore, a large variety of PAEs can be synthetized with a wide range of different physical and chemical properties according to their specific use (Moret, Marega, Conte, & Purcaro, 2012; Russo, Avino, Perugini, & Notardonato, 2015; Staples, 2003). High-molecular weight species, such as bis(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DIMP), are applied as plasticizers for PVC, while low-molecular-weight PAEs, such as dibutyl phthalate (DBP) and diisobutyl phthalate (not considered in this study) are used for cellulose acetate, or as surfactants, emulsifying agents, stabilizers, dispersants, and lubricants (Moret et al., 2012; Russo et al., 2015).

As a consequence of their diffusion, PAEs become process contaminants for food (Cariou et al., 2016; Chou & Wright, 2006; Wormuth, Scheringer, Vollenweider, & Hungerbühler, 2006), including baby foods (Fierens et al., 2012).

Recently, fast food was indicated as an important source of exposure to DEHP and DINP (Zota, Phillips, & Mitro, 2016). Although migration from packaging materials is probably the main source of PAEs contamination in food, PAEs can arise from any step of the productive chain, from the field to the supply chain (Triantafyllou, Akrida-Demertzi, & Demertzis, 2007; Moret et al., 2012).

For the same reason, particular attention must be given to their analysis, as environmental PAEs can give false positives or enhance sample content (Fankhauser-Noti & Grob, 2007; Russo et al., 2015).

PAEs are not chemically bound to the polymeric matrix, but they can be described as a freely mobile phase. The release into the environment and the migration into products through the contact materials are the main ways of their diffusion (Moret et al., 2012; Russo et al., 2015).

Various government agencies, including the EFSA in Europe, and the FDA in the United States, are still assessing the effects of PAEs on human health. These substances are cause of great concern as endocrine disrupting chemicals, mainly related to human reproduction (Committee on the Health Risks of Phthalates, 2008; Owens, 2015). The strongest and most consistent evidence was described for dibutyl phthalate and bis(2-ethylhexyl) phthalate and associated with lower semen quality (Mariana, Feiteiro, Verde, & Cairrao, 2016), although other endocrine functions and different physiological systems are suspected to be involved (Johns, Ferguson, & Meeker, 2016; Mariana et al., 2016).

In order to export distillates produced in other countries to China, the Chinese authority responsible for imports and exports (AQSIQ) has made an analytical report mandatory (circular from the Ministry of Health of 22 January 2013). The report must state the concentrations of three PAEs in accordance with the specification of the law that imposes maximum tolerated concentrations of 0.30 mg/kg for DBP, 1.50 mg/kg for DEHP, and 9.00 mg/kg for DINP. This brings about a severe hindrance to the export of spirits to China, but it is not excluded that other countries might follow the China action imposing a similar trade barrier.

Hence, it is crucial to explore the source of contamination in distilled beverages, as the high percentage of ethanol acts as a solvent for PAEs extraction. Moreover, the fate of different PAEs during the distillation process is so far unknown. Finally, the long ageing (even for decades) in oak casks makes distillates ideal candidates to concentrate PAEs.

In a preliminary study, a robust protocol of analysis for the determination of PAEs in brandies was set up (Montevecchi, Masino, Zanasi, & Antonelli, 2017). The procedure is based on an ultrasound-vortex-assisted dispersive liquid–liquid microextraction (USVADLLME) (Cinelli, Avino, Notardonato, Centola, & Russo, 2013; Russo, Notardonato, Avino, & Cinelli, 2014) originally set up for wine and now optimized for high strength beverages. The method is environmentally friendly because of the limited volume of solvent required, particularly chlorinated (Yan, Cheng, & Liu, 2011). This is also useful because it minimizes the risk of false positive cases due to the presence of phthalates in the solvent.

The results of a screening on PAEs content performed on a historical brandy series (from 1987 to 2014) showed that PAEs concentrations exceeded the limits imposed by the Chinese law (Montevecchi et al., 2017) only in a few of the most aged samples. The content of PAEs in the samples was influenced by the level of PAEs contamination in the raw material (base wines) and by the effect of the concentration that occurred during ageing. However, the repartition into heads, heart, and tails of each PAE during distillation of the base wine is still not investigated. The objective of this paper is to fill this gap, thus providing a tool to improve brandy purification without altering the unique quality of many distillates all over the world.

2. Materials and methods

2.1. Sampling

The base wine (Trebbiano without sulphur dioxide, 10 L) used for distillations was collected by a local winemaker. It was part of a lot used for the process on an industrial scale.

2.2. Chemicals and instruments

All solvents and reagents were of analytical grade. Acetone, dichloromethane, and absolute ethanol were obtained from WVR Srl (Milan, Italy). The pure standards diisobutyl phthalate, bis(2-ethylhexyl) phthalate, diisononyl phthalate, and benzyl butyl phthalate, as well as carborundum, sodium chloride, and sodium hydroxide were purchased from Fluka Sigma-Aldrich® Srl (Milan, Italy). Deionised water was obtained by a Milli-Q purification system (Millipore, Milan, Italy).

2.3. Preparation of materials: solvents, chemicals, and glassware PAE free (PF)

All the solvents used (acetone, dichloromethane, absolute ethanol, and water) were distilled to eliminate the presence of PAEs as described by Montevecchi and coll. (2017). In a few words, all solvents were distilled before use and water, in particular, was distilled on NaOH to prevent steam distillation of PAEs. Then the presence of PAEs was excluded by gas chromatography-mass spectrometry (GC/MS) on concentrated (100:1) solvent samples. Glassware and solid reagents were previously rinsed with acetone PF and were then heated at 400 °C for 4 h. Finally, reagents were stored in PF containers with ground glass stoppers, while glassware was kept separate from dust.

2.4. Pilot distillations

2.4.1. Distillation of base wine spiked with PAEs by a lab still according to the procedure of brandy production

Except for the number of the first distillations (*première chauffe*; only 3 instead of 4), distillation was carried out in accordance with Léauté (1990). A lot of 5.0 L of white Trebbiano base wine was homogenized to suspend yeast lees and divided into three batches (1 L each) to be subjected to distillation. Each batch was spiked with DBP (1 mg in the sample), DEHP (5 mg in the sample), and DINP (20 mg in the sample) and subjected to first distillation (*première chauffe*) in a lab still equipped with a distillation flask (2 L) heated by an electric heating mantle, a column, and a condenser cooled down by cold tap water (Fig. 1).

The distillate was collected in different flasks in accordance with the brandy production method and cut in heads, heart (or *broullis*), and tails (Table 1). After sampling, heads and tails were re-distilled with the succeeding batch of fresh base wine. At the end of the distillation of all the batches of wine, the three *brouillis* were joined and subjected to a second distillation (*bonne chauffe*). During the *bonne chauffe* four fractions were collected (Table 1), heads, heart 1 (or brandy), heart 2 (or secondes), and tails.

2.4.2. Distillation of base wine spiked with PAEs by a lab still and collection of 8 mL fractions

A lot of white Trebbiano base wine measuring 2.5 L was homogenized and divided into two batches (1 L each) to be subjected to distillation. Each batch was spiked with DBP (1 mg in the sample), DEHP (5 mg in the sample), and DINP (20 mg in the sample) and subjected to distillation with the lab equipment described above.

The distilled fractions (8 mL each) were collected in different tubes. The distillation was stopped after collecting 27 fractions (216 mL in total).

2.4.3. Distillation of base wine spiked with PAEs by a lab still with the column filled with Raschig rings and collection of 8 mL fractions

Another lot of wine (2.5 L) was distilled with the same protocol described in section 2.4.2., but the column was filled with Raschig rings in order to improve rectification during distillation.

2.5. Extraction method (Montevecchi et al., 2017)

Samples (8.000 g for wine, stillage, and tails; 1.500 g for heads, heart, brandy, and secondes) were accurately weighed and transferred into a conical tube with ground glass stoppers. Internal standard (benzyl butyl phthalate), up to 8 mL of water (if necessary), and 1.50 g of NaCl were added to each tube. Each sample was vortexed to dissolve the salt. Then dichloromethane PF (160 µL) was added and the mixture was vortexed again for 30 sec. Finally, each tube was sonicated for 10 min (Ultrasonic frequency 37 kHz, Elmasonic S30, Elma Schmidbauer GmbH, Singen, Germany), cooled to 4 °C for 5 min and then centrifuged for 2 min at 5000 rpm. The ready-for-analysis extract was collected from the organic phase at the bottom of the tube.

2.6. GC-MS determination of PAEs

GC-MS analysis was previously described in detail (Montevecchi et al., 2017). In a few words, the extract was injected (splitless mode, 335 °C, splitless time: 30 sec) onto SE52 crossbond capillary column (5% phenyl, 95% methyl polysiloxane; 25 m length, 0.25 mm i.d., 0.25 µm f.t., carrier gas

He at constant flow rate 1 mL/min). Oven temperature: 150 °C for 1 min then up to 330 °C for 2 min, rate 15 °C/min. The injection was performed in splitless mode at 335 °C (splitless time 30 sec), the temperature of the transfer line was set at 330 °C.

The mass spectrometer detector was operated in electron ionization (EI) mode at 70 eV (33-500 *m*/*z*). Identification was carried out by comparing the retention time of the analytes to that of the pure standards (Fig. 2) and confirmed by the qualifying ions (76 and 104 *m*/*z*, 167 and 279 *m*/*z*, 167 and 293 *m*/*z*, for DBP, DEHP, and DINP, respectively). Quantification was carried out by measuring the quantifying ion's (149 *m*/*z*) relative peak area in relationship to that of the internal standard. Each analysis was duplicated.

2.7. HPLC determination of alcohol by volume in fractions collected during distillation

Alcohol by volume (ABV) was determined by a Perkin Elmer HPLC system (Series 200 LCP, Norwalk, U.S.A) equipped with a refractive index detector (RI detector, Series 200). Diluted samples were filtered through 0.45-µm nylon membrane and injected with a 20-µL loop using an injection valve (Rheodyne Inc., Cotati, CA, U.S.A.) onto a Bio-Rad Aminex HPX-87H (Hercules, CA, U.S.A.) hydrogen-form cation exchange resin-based column (300 mm × 7.8-mm i.d.). The column was thermostated at 50 °C into a column oven (Perkin Elmer, Series 200). The solvent system was composed by aqueous H_2SO_4 (pH 2.70), added of CH_3CN (10%). The isocratic elution was carried out with 0.5 mL/min flow. The ethanol retention time was 24 min.

Quantification was carried out by means external of standard method and assessing the linearity of the response. The chromatograms were acquired and processed using the TotalChrom Workstation version 6.2.1 software (Perkin Elmer, Inc.).

3. Results and discussion

3.1. Behaviour of PAEs during distillation of base wine by a lab still

Première chauffe

Concentration of DBP and DEHP in the base wine ranged from 0.012-0.079 mg/kg and 0.005-0.041 mg/kg, respectively. Their concentration was largely below the limits of the Chinese law. DINP was not detected in any sample.

Samples of base wines spiked with standard solutions of PAEs showed concentrations consistent with the amount added (table 2), thus confirming the robustness of the method.

In the stillage, DBP was not detected in any of the cases. On the contrary, about 84 % (average of the 3 distillations) of DEHP remained in the stillage, while DINP did not distil at all, showing very similar figures to the original amount used in spiked samples.

During the first distillation, DBP tended to accumulate in the heart, while only about the 15% of the original DEHP accumulated in the heart (average of the 3 distillations). According to their volatility, DBP behaved as head compound more than DEHP did, and both resulted in the heart with average amounts of 1.1 and 0.81 mg, respectively, although DEHP was 5-times more concentrated in the spiked wine. Finally, they were still present in the tails at an average amount below 0.02 mg. DINP was not detected in any of the distilled fractions (table 2).

Bonne chauffe

In the joint *bruillis*, DBP concentration enhanced 3.5 folds, while DEHP was only about 16 % of the original content (table 2). In the stillage of the *bonne chauffe*, DBP was not detected, while DEHP was as low as 6% of the original amount. As expected, DINP was not detected in any sample.

ABV of *brouillis* (about 40 % v/v) in the *bonne chauffe* is by far higher than in the *première chauffe*. For this reason, in the *bonne chauffe* the distillation was cut in four fractions (instead of three), as for industrial scale process.

DBP and DEHP amounts in the heads (about 79 % ABV) and in the tails (about 0.7 % ABV) were very low. The highest amount of the two substances was concentrated in the two hearts. In the brandy or heart 1 (about 78 % ABV), DBP and DEHP amounts were 0.62 mg and 0.47 mg, respectively, while in the secondes or heart 2 (about 19 % ABV) their amounts were markedly higher. In fact, DBP and DEHP showed values as high as 2.7 mg and 1.0 mg, respectively.

The general analysis of the data clearly showed that DBP, which has the lowest molecular weight (278.35 g/mol) and the lowest boiling point (340 °C), was entirely carried over into the distillate during the *première chauffe*. The phenomenon was even clearer during the *bonne chauffe*, whereas the carrying over of DBP into the distillate occurred mainly during the distillation of the secondes. In this cut the water content was higher to allow a hydrodistillation of DBP. DBP behaviour was similar to those components that are carried over by the water vapour, as most of the volatile compounds during the hydrodistillation process for essential oil production (Léauté, 1990). On the other hand, PAEs were already found as contaminants in essential oils obtained through hydrodistillation, thus confirming that this process is able to carry over and concentrate them during distillation (Di Bella, Saitta, Lo Curto, Salvo, Licandro, & Dugo, 2001; Ricking, Schwarzbauer, & Franke, 2003; Song et al., 2007; Maltese, van der Kooy, & Verpoorte, 2009; Radulović & Blagojević, 2012; Firouzi, Gohari, Rustaiyan, Larijani, & Saeidnia, 2013; Manayi, Saeidnia, Shekarchi, Hadjiakhoondi, Shams Ardekani, & Khanavi, 2014a; Manayi, Kurepaz-mahmoodabadi, Gohari, Ajani, & Saeidnia, 2014b; Wu, Wang, Liu, Zou, & Chen, 2015).
Due to its higher molar mass (418.61 g/mol) and boiling point (estimated at about 426-437 °C), DINP was not carried over at all into the distillate, so it did not represent a concern during the distillation process. Finally, DEHP was in an intermediate position (molar mass 390.56 g/mol and boiling point 385 °C). In fact, it was found in an appreciable amount in the stillage, but it was also present in the secondes, although its solubility in water was as low as 0.00003% (23.8 °C).

3.2. Behaviour of PAEs during distillation of base wine by a lab still (8-mL fractions)

Consistently with the previous experiment, PAEs amounts were very low in the base wine. At the end of distillation, DBP was not detected in the stillage, DEHP amount was reduced and, finally, DINP amount was constant.

The analysis of the 27 fractions collected during distillation showed that DBP (Fig. 3A) was even carried over at the early stage. Its maximum amount was reached in the eleventh fraction (about 0.27 mg) and, after this, its amount was reduced until it disappeared completely in the twentieth fraction.

DEPH (Fig. 3B) achieved its highest amount in the eleventh fraction (about 0.09 mg), and thereafter showed fluctuating values up to the end of the process. DINP was not detected in any fraction.

These data suggested that DBP achieved its highest amount at the end of the ethanol carry-over and during the shift of the boiling point of the sample (dotted line in Fig. 3A). The greatest part of the DBP was carried over into the distillate when full grade was reached and was sharply reduced when the ethanol disappeared.

Even if the DEHP profile is less regular, it behaved in a quite similar way, showing a clear peak at almost the same point of the distillation process as for DBP. From then onwards, DEHP concentration was less regular. However, two observations must be pointed out: i) when volumes are so tiny a little spurt or a single drop can make the difference; ii) DEHP is a very high boiling substance and this could explain some fluctuation in its distillation.

3.3. Behaviour of PAEs during distillation of base wine by a lab still (8-mL fractions) with rectification (column filled with Raschig rings)

The previous experiment was repeated using the same conditions, but the column was filled with Raschig rings in order to evaluate the effect of the rectification on PAEs behaviour. In the stillage, DBP was not detected, while DINP showed values similar to the previous experiment. Conversely, DEHP showed higher amounts in the stillage in comparison with what was detected in the previous test.

The DBP trend showed that it was present starting only from the eighth fraction (Fig. 4A), then it achieved its maximum amount in the tenth fraction (about 0.37 mg) and, finally, it had already almost zeroed in the eighteenth fraction.

For DEHP (Fig. 4B), its presence started from the eighth fraction, as well, and reached the maximum amount in the eleventh fraction (about 0.18 mg), and then it dropped down without zeroing at all. DINP was never detected in any fraction.

As a matter of fact, rectification allowed the modification of the trend of DBP and DEHP carry-over. For both of them there was a retarded carry-over, but it was concentrated in a smaller volume, especially for DBP. This effect can be exploited to reduce PAEs contamination in the secondes, the fraction where DBP and DEHP accumulated during the *bonne chauffe*. Secondes are considered a valuable fraction for ethanol concentration (about 19 % ABV) and aroma compounds, and for this reason they are kept to be reintroduced in the pot still during the subsequent *bonne chauffe*. As a consequence of this, manufacturers can take advantage of the rectification step on the secondes in order to eliminate only the most contaminated part of them and save the rest.

4. Conclusions

The results highlighted how the chemical nature of the individual PAE influenced its own behaviour during the distillation process. DBP was entirely found in the distillate, while DINP accumulated in the stillage. DEHP showed an intermediate behaviour, since it was only partially carried over into the distillate.

The most impressive phenomenon was highlighted during the *bonne chauffe*, whereas DBP and DEHP accumulated in the secondes more than in the heart 1. A rectification step of the secondes can allow a considerable reduction of PAEs concentration in order to reintroduce this valuable fraction cleaner in the distillation process, thus improving the quality of brandies.

Considering the behaviour of DBP and DEHP, it is very difficult to suggest modification of the distillation process without impairing the quality of brandies. The prevention of PAEs wine contamination seems to be the only way to have a low content of PAEs in the brandy. Pipelines used for the pouring of brandy can be a source of PAEs: plastic hosepipes and other plastic objects should be kept separate and the contact with distillates avoided.

Acknowledgments

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Figure captions

Fig. 1. Lab still equipped with a distillation flask (2 L) heated by an electric heating mantle, a column, and a condenser cooled down by cold tap water.

Fig. 2. GC trace of a wine sample spiked with standard solutions of PAEs.
DBP = dibutyl phthalate; DEHP = bis(2-ethylhexyl) phthalate; DINP = diisononyl phthalate. IS = internal standard (BBP, benzyl butyl phthalate).

Fig. 3 A. Trends of amounts (expressed in mg) of DBP in the 27 fractions (8 mL each) collected in the base wine pilot distillation. **B**. Trends of amounts (expressed in mg) of DEHP in the 27 fractions (8 mL each) collected in the base wine pilot distillation.
Dotted lines indicate the shift of the boiling point of the sample from 78 °C toward the boiling point of water.

Fig. 4 A. Trends of amounts (expressed in mg) of DBP in the 27 fractions (8 mL each) collected in the base wine pilot distillation with Raschig rings. **B**. Trends of amounts (expressed in mg) of DEHP in the 27 fractions (8 mL each) collected in the base wine pilot distillation with Raschig rings.
Dotted lines indicate the shift of the boiling point of the sample from 78°C toward the boiling point of water.

Table(s)

Table 1 – Schematization of fractionation during distillation

Première chauffe				
Wine (mL)	Heads (mL)	Heart or *Brouillis* (mL)		Tails (mL)
1000	4	280		60
1064*	4	280		60
1064*	4	280		60
Bonne chauffe				
Brouillis (mL)	Heads (mL)	Heart 1 or Brandy (mL)	Heart 2 or Secondes (mL)	Tails (mL)
840	10	280	240	60

* Comprehensive of 1000 mL of wine, 4 mL of heads and 60 mL of tails of the previous distillation.

Table 2

Amount of PAEs (DBP, DEHP, and DINP) expressed in mg and alcohol by volume recorded during the distillation tests.

		DBP (mg ± st. dev.)	DEHP (mg ± st. dev.)	DINP (mg ± st. dev.)	ABV (% v/v ± st. dev.)
Première chauffe					
1	Wine	0.015 (±0.004)	0.008 (±0.002)	N.D.	9.11 (±0.02)
	Wine + PAEs	0.95 (±0.13)	4.74 (±0.28)	19.4 (±1.3)	9.13 (±0.04)
	Stillage	N.D.	3.94 (±0.17)	19.2 (±1.3)	N.D.
	Heads	0.001 (±0.000)	0.009 (±0.000)	N.D.	66.93 (±0.61)
	Heart	0.94 (±0.07)	0.78 (±0.05)	N.D.	36.96 (±0.45)
	Tails	0.009 (±0.000)	0.017 (±0.000)	N.D.	0.69 (±0.01)
2	Wine	0.012 (±0.003)	0.005 (±0.002)	N.D.	9.54 (±0.16)
	Wine + PAEs	1.11 (±0.08)	5.19 (±0.70)	19.2 (±0.5)	9.57 (±0.21)
	Stillage	N.D.	4.32 (±0.20)	19.8 (±1.7)	N.D.
	Heads	0.002 (±0.000)	0.009 (±0.000)	N.D.	72.39 (±0.37)
	Heart	1.10 (±0.08)	0.85 (±0.07)	N.D.	38.70 (±0.07)
	Tails	0.008 (±0.000)	0.013 (±0.001)	N.D.	0.70 (±0.03)
3	Wine	0.079 (±0.004)	0.041 (±0.010)	N.D.	9.41 (±0.29)
	Wine + PAEs	1.19 (±0.05)	5.31 (±0.21)	19.9 (±1.2)	9.48 (±0.33)
	Stillage	N.D.	4.49 (±0.28)	19.8 (±1.6)	N.D.
	Heads	0.004 (±0.000)	0.008 (±0.000)	N.D.	62.22 (±0.32)
	Heart	1.18 (±0.06)	0.79 (±0.05)	N.D.	38.87 (±0.52)
	Tails	0.006 (±0.000)	0.010 (±0.000)	N.D.	0.67 (±0.01)
Bonne chauffe					
	Joint Brouillis	3.32 (±0.05)	2.44 (±0.33)	N.D.	38.29 (±0.38)

Stillage	N.D.	0.95 (±0.68)	N.D.	N.D.
Heads	0.001 (±0.000)	0.005 (±0.000)	N.D.	78.64 (±0.02)
Brandy	0.62 (±0.05)	0.47 (±0.04)	N.D.	77.64 (±0.01)
Secondes	2.69 (±0.17)	1.01 (±0.06)	N.D.	18.66 (±0.20)
Tails	0.008 (±0.000)	0.016 (±0.002)	N.D.	0.66 (±0.03)

st. dev. = standard deviation; ABV = alcohol by volume; N.D. = not detected.

Figure(s)
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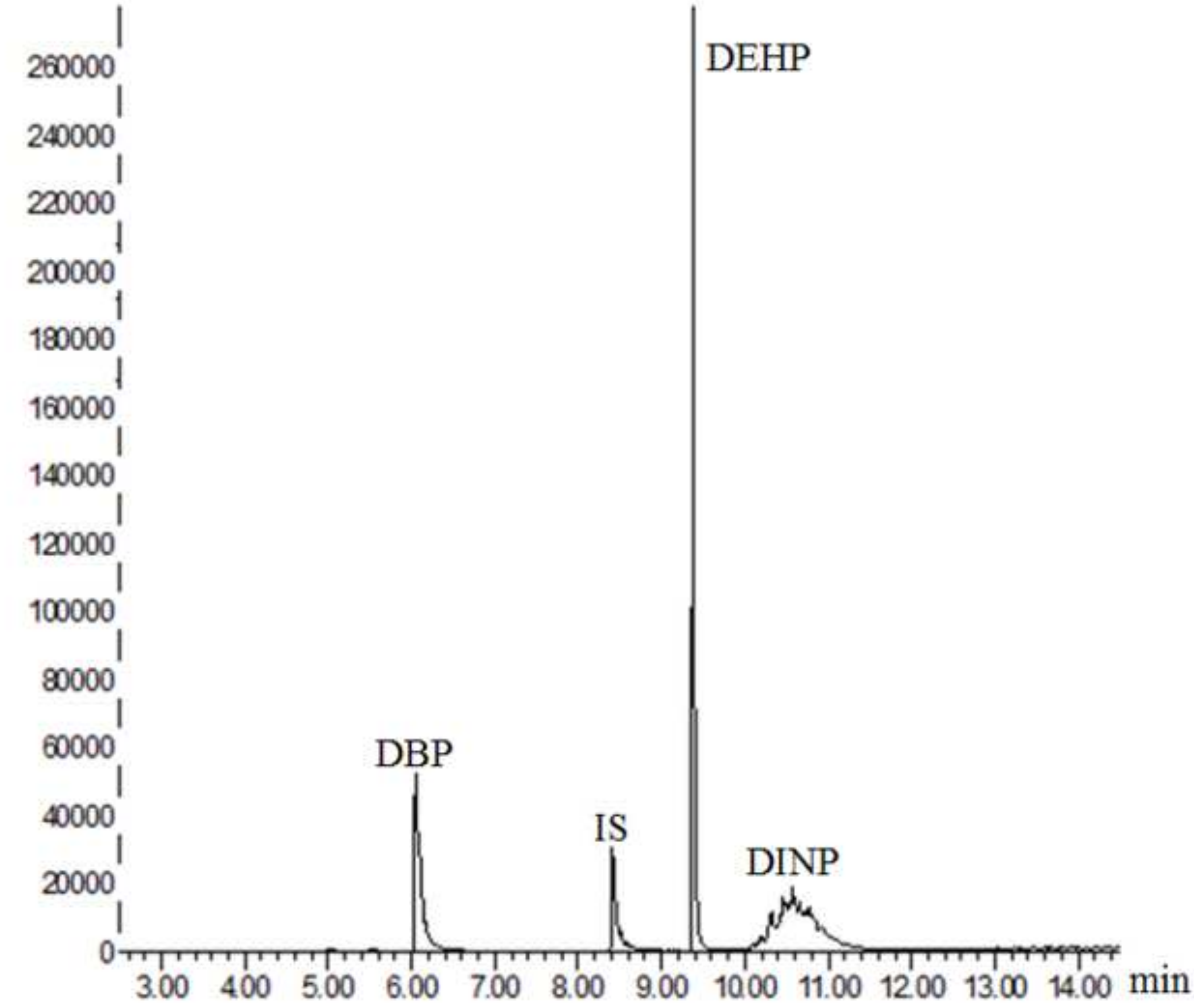

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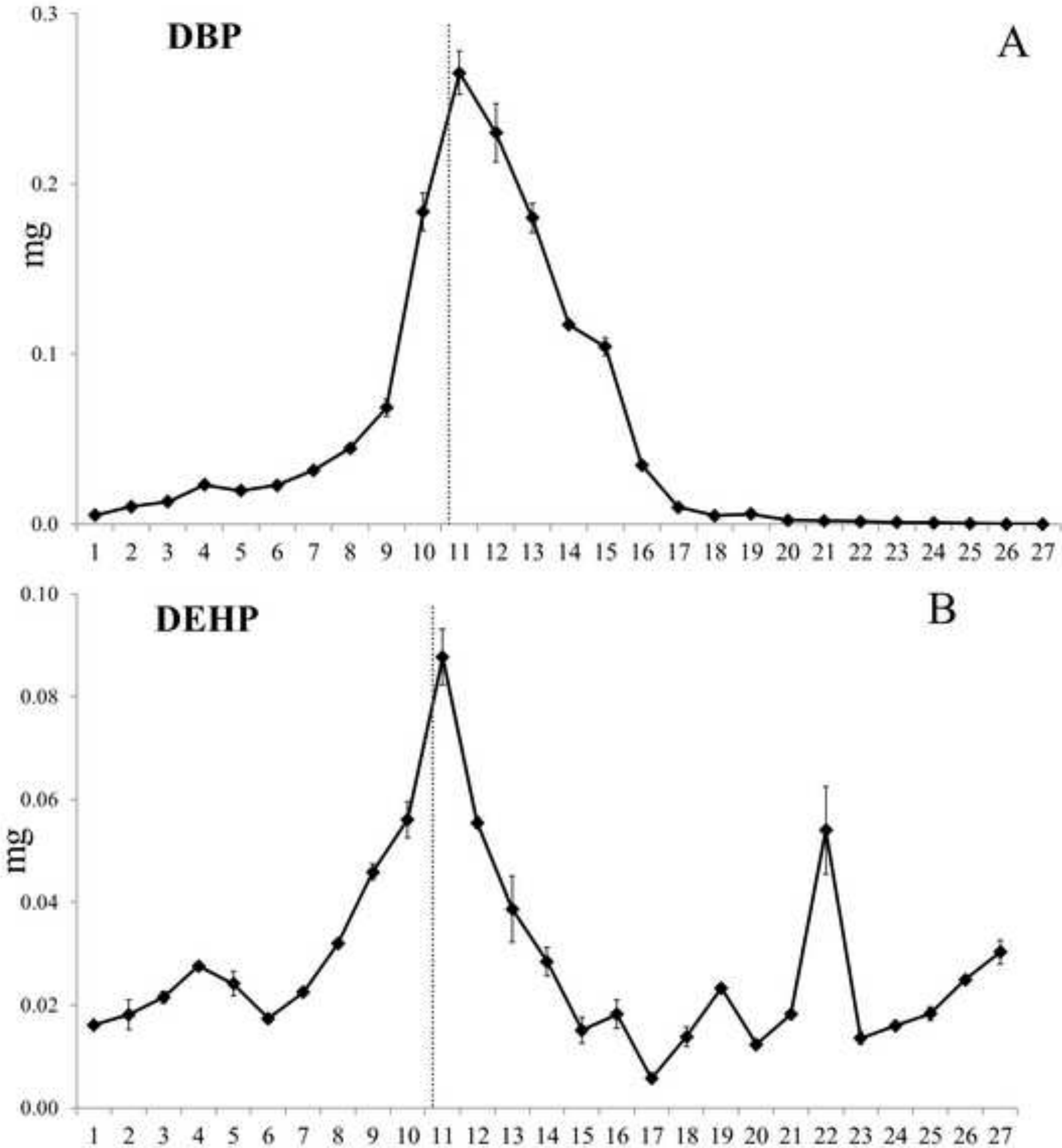

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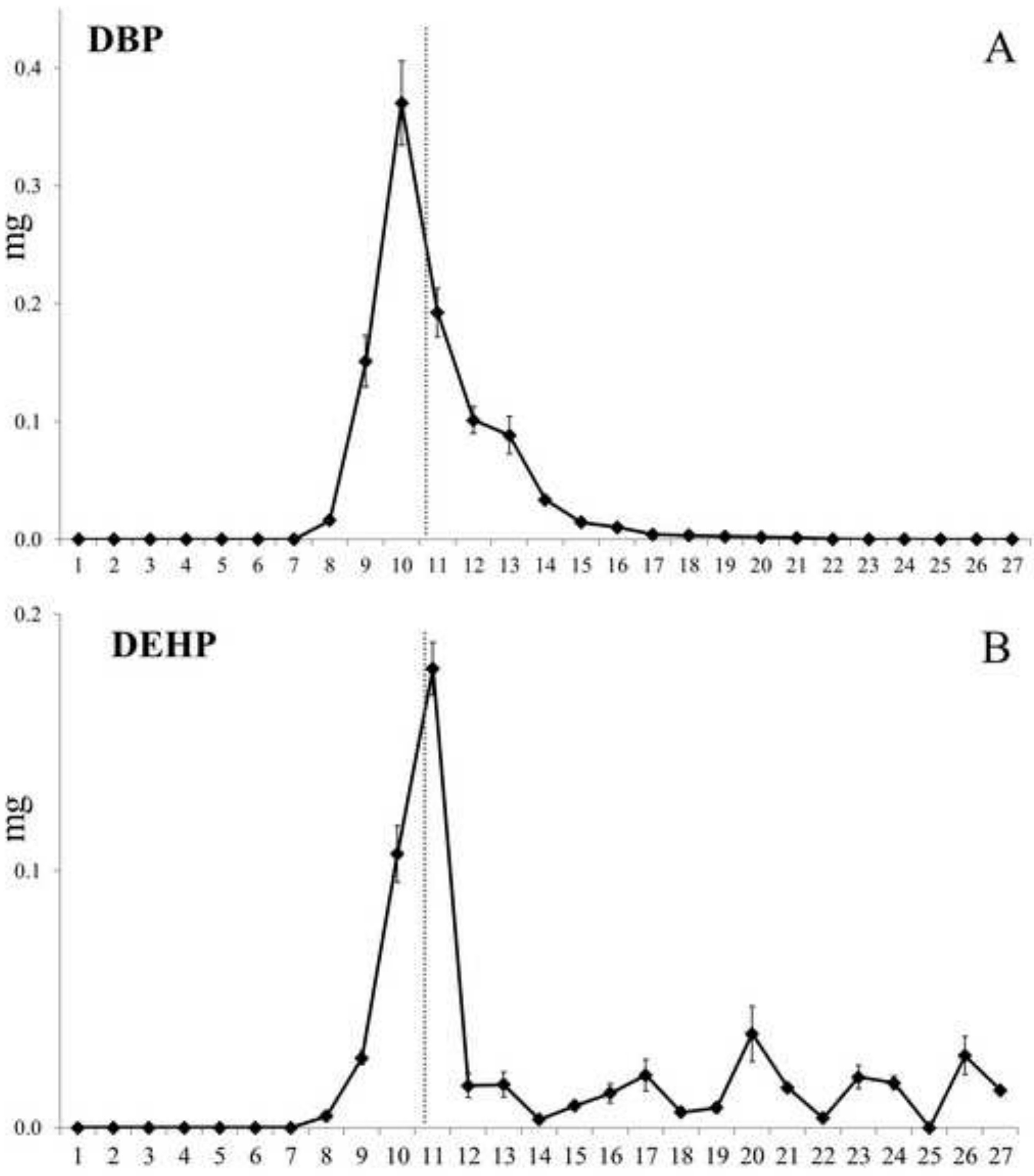

DBP
A
mg
0.4
0.3
0.2
0.1
0.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
DEHP
B
mg
0.2
0.1
0.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27