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THE BEHAVIOUR OF TENAX AS FOOD SIMULANT IN THE MIGRATION OF POLYMER ADDITIVES FROM FOOD CONTACT MATERIALS BY MEANS OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND PARAFAC

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HIGHLIGHTS

- Migration of polymer additives from food contact materials into Tenax was studied
- PARAFAC enabled the unequivocal identification in the presence of coeluting compounds
- Some of the *m/z* ratios of the coeluting interferents were shared with the analytes
- Tenax as a suitable food simulant is questioned considering its adsorption capability
- BP and DiBP have migrated from PVC film and from PP coffee capsules

Abstract

The migration of benzophenone (BP), an antioxidant (2,6-di-tert-butyl-4-methyl-phenol (BHT)) and three plasticizers (diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP)) from different food contact materials into Tenax as food simulant was studied. The packaging materials analysed were: polyethylene (PE) and polyvinyl chloride (PVC) cling-films, paper bread bag, brown paper popcorn bag intended to be heated in a microwave oven and polypropylene (PP) coffee capsules. The analysis was carried out using PARAFAC and PARAFAC2 decompositions and gas chromatography/mass spectrometry (GC/MS), being DiBP-d_4 the internal standard. Tenax has been used as food simulant for specific migration of dry foodstuffs according to Commission Regulation (EU) 10/2011.

PARAFAC and PARAFAC2 decompositions enabled the unequivocal identification and quantification of all the analytes despite some of the *m/z* ratios of the coeluting interferents were shared with the analytes. Otherwise, the presence of the analytes could not have been ensured according to the EU legislation in force.

BHT, DiBP and DEHA were contained in the Tenax blanks in some of the analyses. The amount of BP and DiBP migrated from the PVC film was 83.53 µg L^{-1} and 31.30 µg L^{-1} , respectively; whereas 71.62 µg L^{-1} of BP and 27.45 µg L^{-1} of DiBP migrated from the PP coffee capsules. None of the analytes were

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detected above the capability of detection in the non-spiked migration samples of the rest of the food contact materials analysed.

The efficiency of Tenax as an adequate food simulant has also been studied through the values of its adsorption capability which were different depending on the analytes and the materials. In the spiked migration samples, these values ranged from 25.33% to 99.37%.

Keywords: Tenax; Plasticizers; Benzophenone*;* PTV-GC/MS; PARAFAC; Migration test.

1. Introduction

Different packaging materials such as plastic, paper, board, ceramic, glass and metal are in contact with foodstuffs [1]. These materials contain different compounds that could migrate into food by different transfer mechanisms: direct contact with the food or indirectly through the gas phase between the material and the food surface [2,3]. All materials and articles intended to come into contact with food are called food contact materials [4] which represent a potential source for human exposure to chemicals [5] since the compounds transferred to the food could cause health damage when ingested by consumers [3]. The migration mechanism of the additive could be influenced by the nature of the food, the food-additive interactions and time or temperature storage conditions. In addition, the migration of a compound into food depends on its initial concentration in the packaging product [6].

Regulation (EC) 1935/2004 [7] states that the constituents of food contact materials must be sufficiently inert so as not to transfer substances into food in quantities that could endanger human health or bring about unacceptable changes in composition or characteristics of foodstuffs. In addition, Commission Regulation (EU) 10/2011 [8] establishes the specific migration limits (SML) for many constituents of the plastic materials as the maximum permitted amount of a given substance released from a material or article into food or food simulants. These SMLs are established according to toxicological evaluations carried out by the European Food Safety Authority. .

Commission Regulation (EU) 10/2011 [8] also establishes different food simulants depending on the characteristics of the foodstuff to replace. One of those food simulants is Tenax (food simulant E in [8] for specific migration from plastics into dry foodstuffs) whose trade name is poly(2,6-diphenyl-p-phenylene oxide).

However, the use of Tenax presents several disadvantages. The high cost of Tenax is the major drawback in migration testing using this simulant [3,9,10,]. In addition, static electricity caused by friction or laboratory gloves makes it difficult to manage [11]. Tenax also contains impurities so a cleaning step prior to its use must be performed [12]. Several studies have compared the migration into Tenax and into real dry foods such as pasta, sugar, flour, milk powder, raisins, rice, fruits and vegetables. These studies concluded that the migration into Tenax is faster and presents higher values than into real food, so the results are overestimated when this simulant is used [13,14,15]. For this reason, the use of Tenax as food simulant could lead to false positive results. On the other hand, Tenax should not be recommended as a food simulant for temperature up to 150ºC. In this case, the adsorbent Porapak could be used [16,17,18]. The European Reference Laboratory for Food Contact Materials (EURL-FCM) performed an

interlaboratory comparison about the identification and quantification of substances spiked in Tenax. Only 48% of the national reference laboratories identified correctly the substances [11] despite Tenax could lead to false positive results. Therefore, its usage may present difficulties due to all these reasons.

The food contact material is placed in contact with the food simulant in a manner representing the worst of the foreseeable conditions according to the conditions defined in Commission Regulation (EU) 2016/1416 [19] which corrects the Commission Regulation (EU) 10/2011 [8] to test for migration of materials not yet in contact with food.

The additives migrated from plastic or paper materials into Tenax can be extracted with different organic solvents such as hexane [2,11,12], acetone [20,21,22] and ethanol [9,14,15].

Plastic materials are regulated by Commission Regulation (EU) 10/2011 [8] which has been modified throughout the years, being its last modification of June 2018. Some food contact materials have not been covered by specific European legislation yet such as paper and board [1,5] although they are the most commonly used food packaging materials together with plastic materials [1]. The European Food Safety Authority (EFSA) has created a document about the migration from non-plastic food contact materials [23]. Paper and board can be treated as monolayer plastic packaging materials because the diffusion rate decreases with the increase in the molecular weight of the migrants [24] although the transfer into the foodstuff could happen much faster in the paper material than the migration from plastics [16].

Monomers and starting substances, catalysts, solvents and additives are included as substances that may migrate from plastic materials. Different additives are used to improve the elasticity, flexibility, colour, resistance and durability of plastics [25]. Polymer additives used in plastics include antioxidants, antifogging agents, slip additives, plasticizers, heat stabilisers, dyes and pigments [26]. Phthalates and adipates are the most commonly used plasticizers in polyvinyl chloride (PVC), polypropylene (PP) and polyethylene (PE) [6,10,27,]. In the manufacture of paper material, different additives such as fillers, starch, biocides, fluorescent whitening agents, grease-proofing agents and polymers such as PE or waxes are used [26].

Several food contact materials such as paper, cardboard, plastic, metal, glass jars and tetra brick contain phthalates [28]. However, paper and board do not contain phthalates as plasticizers; but lacquers, adhesives, and printing inks may contain these compounds [9,10,29,]. Phthalates, plasticizers and bis(2-ethylhexyl) adipate (DEHA) as adipate compounds are endocrine disruptors which adversely affect hormonal function. DEHA is the mainly adipate added to PVC cling-films [25,28,30,]. All these compounds interfere in disorders such as different types of cancer and physiological processes such as masculinization, morphological development of urogenital system and secondary sexual traits. In addition, these compounds cause the development of obesity and glucose metabolism disorders and the exposure of infants is mainly due to maternal breastfeeding [25,31,32].

This work studies the migration of three plasticizers (diisobutyl phthalate (DiBP), DEHA and diisononyl phthalate (DiNP)) together with benzophenone (BP) and the antioxidant (2,6-di-tert-butyl-4-methyl-phenol (BHT)) from different food contact materials into Tenax. The packaging materials analysed were: (i) plastic materials such as PE and PVC cling-films, and PP coffee capsules; (ii) paper materials such as paper bread bag and brown paper popcorn bag intended to be heated in a microwave oven.

Several notifications in relation to the migration of those three plasticizers, BHT and benzophenone from food contact materials have been sent by different EU countries which have transmitted them to the Rapid Alert System for Food and Feed (RASFF) [33]. From August 2004 to June 2017, RASFF has reported 5 notifications for BHT; 2 for DiBP (one of them from PVC cling-film); 13 for DEHA (nine of them from cling-

film); 42 for DiNP (mostly from glass jars); and 23 for BP (usually from carton boxes which contain cereals). DEHA has been found at 121 mg kg^{-1} and 24.2 mg $(dm^2)^{-1}$ from cling-film, while the amount of BP found from carton boxes containing cereals was 81 mg kg^{-1}. For this reason, the unequivocal identification and quantification of plasticizers, BHT and benzophenone that have migrated from food contact materials are necessary.

In this work, the multiresidue analysis of BHT, BP, DiBP, DEHA and DiNP, using DiBP-d_4 as internal standard (IS), was carried out by means of gas chromatography/mass spectrometry (GC/MS) and parallel factor analysis (PARAFAC) decomposition. The uniqueness property of PARAFAC makes it possible to identify compounds unequivocally by their chromatographic and spectral profiles as laid down in some official regulations and guidelines [34,35,36], even if a coeluent that shares ions with the analyte of interest is present [37,38]. To protect human health, the criteria established in Decision 2002/657/EC for residues of veterinary medicinal products 35] have been followed throughout this work since its requirements are stricter than the ones established in [34]. In this case, at least a minimum of 3 identification points is needed for the confirmation of each compound. The behaviour of Tenax was also evaluated in this work to study its efficiency and adsorption capability as food simulant.

2. Material and methods

2.1. Chemicals

Benzophenone (CAS no. 119-61-9; purified by sublimation), 2,6-di-tert-butyl-4-methyl-phenol (CAS no. 128-37-0), diisobutyl phthalate (CAS no. 84-69-5), diisobutyl phthalate-3,4,5,6-d_4 (CAS no. 358730-88-8; analytical standard), bis(2-ethylhexyl) adipate (CAS no. 103-23-1) and diisononyl phthalate (CAS no. 28553-12-0; ester content ≥ 99%, mixture of C_9 isomers), all of 99% or higher purity, were purchased from Sigma-Aldrich (Steinheim, Germany).

Acetone (CAS no. 67-64-1) and n-hexane (CAS no. 110-54-3) for liquid chromatography Lichrosolv® were from Merck KGaA (Darmstadt, Germany).

Tenax TA (refined), particle size 60-80 mesh, was purchased from Supelco (Bellefonte, USA) and cleaned up prior to its use by Soxhlet extraction. Tenax taken from only one batch was used.

2.2. Standard solutions

Stock solutions of DiBP, DEHA and DiNP at 2000 mg L^{-1}, of BHT at 1500 mg L^{-1}, of BP at 2300 mg L^{-1} and of DiBP-d_4 at 700 mg L^{-1} were prepared individually in hexane. These solutions were stored in crimp vials at 4ºC and protected from light. Intermediate solutions were prepared from the stock solutions by dilution in the same solvent. All these samples were under gravimetric control. Only laboratory glassware thorough cleaned was used and plastic consumables were avoided as far as possible. Table 1 contains the number and type of the samples analysed together with the concentration ranges of each analyte in each experimental stage of this work.

2.3. Plastic and paper samples

For migration studies, five different food contact materials were purchased at local stores (Burgos, Spain). These materials were: i) PE cling-film, ii) paper bread bag, iii) PVC cling-film, iv) brown paper popcorn bag, which is referred to the bag used for making popcorn in a microwave oven (this paper was not coated with any plastic layer) , and v) PP coffee capsules. All of them were intended to come into contact with dry foodstuffs.

2.4. Experimental procedure

2.4.1. Cleaning of Tenax

Prior to its use, 5 g of Tenax was placed into a cellulose thimble and cleaned with 65 mL of acetone in a Soxhlet apparatus for 6h. This equipment had six places where Tenax could be cleaned at the same time so a total of 30 g of Tenax was cleaned. The Tenax contained in each thimble was placed into a Petri dish which was then closed and put under the fume hood. The Petri dishes were finally placed into an oven at 160°C for 6h. The Tenax was stored in a glass desiccator after reaching room temperature until its use. The amount of Tenax which had been cleaned was mixed before the analysis to eliminate the variability.

2.4.2. Migration test sample preparation

Each food contact material was cut into round pieces with a diameter of 48 mm and each piece was placed into a Petri dish except for the PP coffee capsules since the migration test was carried out with the whole coffee capsules and Petri dishes were not used in this last case. The paper popcorn bag was cut where the material had not been yet in contact with the popcorn. The spiked migration samples were used to evaluate the adsorption capability of Tenax. These samples were prepared by adding 70 µL of a solution containing the analytes at the appropriate concentration to each round piece and inside the PP coffee capsule to obtain a final concentration of 50 µg L^{-1} of BHT, BP, DiBP and DEHA, and 2 mg L^{-1} of DiNP. These spiked samples were kept for 2 h before adding Tenax. The same volume of hexane (70 µL) without the analytes was added to prepare the non-spiked migration samples. Next, 1 g of clean Tenax was distributed over the sample to cover it completely and the Petri dish was closed. In the case of the PP coffee capsule, this amount of Tenax was put inside it. The Petri dishes and the PP coffee capsules were wrapped with aluminium foil carefully. The migration test was conducted in an oven under the following conditions of contact: 60ºC for 10 days for the popcorn bag, the PE and PVC films, and 70ºC for 3 days for the bread bag. In the case of the PP coffee capsules, two different conditions of contact were considered: 100ºC for 5 min and 100ºC for 10 days (severe conditions). At the end of each migration period, the samples were removed from the oven and allowed to reach room temperature.

2.4.3. Extraction procedure of the Tenax

The Tenax contained in the Petri dish or in the PP coffee capsule after the corresponding migration test (1 g) was transferred carefully into a 40-mL vial and 10 mL of hexane was added. The vial was shaken at 1500 rpm for 7 min 30 s using a magnetic stirrer and during that time the stirrer was stopped each 30 s to prevent the adhesion of Tenax to the glass (as explained in [39]) and it was turned on again after 5 s. Then, the vial was left to settle for 5 min. The hexane was decanted through a fritted funnel with a glass microfiber filter placed into a new 40-mL vial. The extraction procedure was repeated using once again 10

mL of hexane and the whole extract was collected in a 20-mL volumetric flask. The internal standard was added before completing to the mark, with a final concentration of 25 µg L^{-1}. A portion of the extract was transferred to a 2-mL amber glass vial for the injection in the GC/MS system.

2.5. Instrumental

An apparatus for Soxhlet extraction DET. GRAS N with 6 places (JP Selecta S.A., Barcelona, Spain) and the cellulose thimbles PRAT DUMAS (26 mm inner diameter, 30 mm outer diameter, 60 mm height) (Couze-et-Saint-Front, France) were used for the cleaning of Tenax. The drying of the simulant and the migration testing were performed in an oven Conterm (JP Selecta S.A., Barcelona, Spain). The migration cells were Duroplan Petri dishes made of Duran® borosilicate glass (60 mm outer diameter × 20 mm height) which were obtained from Sigma-Aldrich (Steinheim, Germany).

Fritted funnels made of borosilicate glass with a diameter of 47 mm (Boroglass S.L., Barcelona, Spain) were used in the extraction step together with the Whatman® glass microfiber filters (GF/A grade, 47 mm diameter) which were purchased from GE Healthcare (Little Chalfont, UK). A magnetic stirrer GERSTEL 20 Position Twister Stir Plate (Mülheiman der Ruhr, Germany) was also used.

Analyses were performed on an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrometer detector (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was achieved with an Agilent HP-5MS Ultra Inert column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The injection system consisted of a programmed temperature vaporizer (PTV) inlet with a septumless head CIS 6 from GERSTEL GmbH & Co. KG (Mülheim an der Ruhr, Germany) equipped with a straight-with-notch quartz glass liner. The injections were carried out using the MultiPurpose Sampler MPS2XL from GERSTEL with a 10 µL syringe.

2.6. GC/MS analysis

Helium was used as the carrier gas at a constant flow of 1.3 mL min^{-1} and the PTV inlet operated in the cold splitless mode. The initial pressure was set at 10.121 psi. Two washings of the syringe with acetone and other two washings with hexane were performed before and after every injection. The injection volume was 1 µL which was injected at a controlled speed of 1 µL s^{-1} with an injection penetration of 40 mm. The inlet temperature was held at 55ºC for 0.1 min during the injection and then ramped at 12ºC s^{-1} up to 270ºC, which was held for 15 min. The septum purge flow rate was 3 mL min^{-1} while the purge flow rate through the split vent was fixed at 30 mL min^{-1} (from 0.6 min to 2 min) and 20 mL min^{-1} (after 2 min).

The GC oven temperature was maintained at 40ºC for 0.6 min after injection and then ramped at 20ºC min^{-1} to 250ºC, which was held for 1 min and next increased at 10ºC min^{-1} to the final temperature of 290ºC, which was held for 3 min. The run time was 19.1 min. A post-run step was performed at 300ºC for 4 min.

The mass spectrometer operated in the electron impact (EI) ionization mode at 70 eV. Data were acquired in single ion monitoring (SIM) mode after a solvent delay of 8 min. Five acquisition windows were considered: i) for BHT peak (start time: 8 min, ion dwell time: 30 ms), the *m/z* ratios recorded were 91, 145, 177, 205 and 220; ii) for BP peak (start time: 8.80 min, ion dwell time: 30 ms) the diagnostic ions were 51, 77, 105, 152 and 182; iii) for DiBP and DiBP-d_4 peaks (start time: 9.80 min, ion dwell time: 10 ms), the *m/z* ratios selected for DiBP were 104, 149, 167, 205 and 223, while the diagnostic ions for DiBP-

d_4 were 80, 153, 171, 209 and 227; iv) for DEHA peak (start time: 12 min, ion dwell time: 30 ms), the *m/z* ratios recorded were 112, 129, 147, 241 and 259; and v) for DiNP peak (start time: 14.60 min, ion dwell time: 25 ms), the diagnostic ions were 57, 127, 149, 167, 275 and 293. The transfer line temperature was set at 300°C, whereas those of the ion source and the quadrupole were 230°C and 150°C, respectively.

2.7. Software

MSD ChemStation version E.02.01.1177 (Agilent Technologies, Inc.) with Data Analysis software was used for acquiring and processing data. PARAFAC and PARAFAC2 decompositions were performed with the PLS_Toolbox [40] for use with MATLAB [41] (The MathWorks, Inc.). The regression models were fitted and validated using STATGRAPHICS Centurion XVI [42]. Decision limit (CCα) and capability of detection (CCβ) were determined using the DETARCHI program [43].

3. Theory

3.1. PARAFAC and PARAFAC2 decompositions

GC/MS data can be arranged in a three-way array $\underline{\mathbf{X}}$ (of dimension $I \times J \times K$), considering the I elution times and the abundances measured at J *m/z* ratios for each chromatographic peak for K samples. This array can be analysed with the PARAFAC decomposition technique which is used with multiway data [44]. The trilinear PARAFAC model is described in Eq. (1):

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk}\ , \quad i = 1, 2,\ldots, I;\ \ j = 1, 2,\ldots, J;\ \ k = 1, 2, \ldots, K \qquad (1)$$

where F is the number of factors, $\mathbf{a}_f$, $\mathbf{b}_f$ and $\mathbf{c}_f$ are the loading vectors of the chromatographic, spectral and sample profiles, respectively, of the f-th compound and e_{ijk} are the residuals of the model. GC/MS data are trilinear if the experimental three-way array is compatible with Eq. (1).

The core consistency diagnostic (CORCONDIA) [45] measures the trilinearity degree of the experimental three-way array when F ≥ 2. If the three-way array is trilinear, then the maximum CORCONDIA value of 100 is found. The PARAFAC least squares solution is unique when the three-way array is trilinear and the appropriate number of factors has been chosen to fit the PARAFAC model [38].

PARAFAC2 is used to correct deviations from trilinearity when shifts in the retention time of the analytes from sample to sample appear in the chromatogram [46,47]. In this case, PARAFAC2 applies the same profiles ($\mathbf{b}_f$, f = 1,…,F) along the spectral mode and allows the chromatographic mode to vary from one matrix to another. PARAFAC2 model is described in Eq. (2):

$$\underline{\mathbf{X}} = \left(x_{ijk}\right) = \left(\sum_{f=1}^{F} a_{if}^{k} b_{jf} c_{kf} + e_{ijk}\right),\ \ i = 1, 2,\ldots, I;\ \ j = 1, 2,\ldots, J;\ \ k = 1, 2, \ldots, K \qquad (2)$$

where the superscript k is added to account for the dependence of the chromatographic profile on the k-th sample.

The shift of the retention time is limited in regulated analyses. For the unequivocal identification in these analyses [34], the relative retention time of the analyte shall correspond to that of the reference sample within a tolerance of ±0.5% for GC. Therefore, in this work, the PARAFAC or PARAFAC2 decomposition was performed with a window of scans around the retention time of each analyte. No peak alignment was carried out because in this case it would be impossible to apply the criterion of identification of the retention time.

The non-negativity constraint could be imposed in the three profiles if necessary to obtain the PARAFAC and PARAFAC2 model.

The outlier data in PARAFAC and PARAFAC2 models can be detected by using Q residuals and Hotelling's T^2 statistics. If both statistics exceed their threshold values in a sample, that sample should be rejected and PARAFAC or PARAFAC2 model should be estimated again.

The unequivocal identification and quantification of the analyte of interest in the presence of unknown interferents are possible with PARAFAC and PARAFAC2 since the interferent(s) appear as new factor(s) without affecting the rest due to the second-order advantage. This is extremely useful in GC/MS analyses when a single quadrupole is used since a coeluent that shares ions with the analyte of interest could be present.

4. Results and discussion

4.1. Tolerance intervals for the unequivocal identification of the analytes

In this work, the requirements for the unequivocal identification of the analytes in the analysis of food contact materials laid down in EUR 24105 EN [34] were followed and at least 3 *m/z* ratios should meet the identification conditions as stated in [35]. To establish the permitted tolerance intervals, six reference standards were prepared and analysed. Three of them contained the analytes at three different concentration levels and the IS at a fixed concentration, whereas the three remaining standards contained the analytes at a fixed concentration and the IS at three concentration levels. Table 1 (first row, columns 8-13) collects the concentration ranges of each analyte in these standards. The performance of the GC/MS system was tested with the injection of three system blanks (no solvent) at the beginning, middle and end of the analytical sequence and a solvent blank without IS (only hexane). The chromatograms obtained from these 10 samples were fragmented around the retention time of each analyte after baseline correction. Next, three-way arrays containing the data matrices of the reference standards, system and solvent blanks were built for each analyte. Only a three-way array was considered for DiBP and DiBP-d_4 peaks. The dimensions of the five three-way arrays are specified in Table S1 of the Supplementary Material (first row, columns 3-7), while the features of the model estimated from the PARAFAC decomposition of each three-way array are included in the second row of this table. In the case of BP, a PARAFAC2 model was considered due to the shifts in the retention time of this analyte in those samples. The chromatographic, spectral and sample profiles of this two-factor model for BP and the compound that coeluted with it are shown in Fig. 1. The *m/z* ratios 51, 77, 105 and 152 recorded for BP were also shared with the interferent (see Fig. 1(b)) mainly present in three reference samples (samples 5, 7 and 8 in Fig. 1(c)). The sample loadings (Fig. 1(c)) were numerically high since the third profile is not normalized in the PARAFAC2 decomposition. The sample loadings of three reference standards (samples 7, 8 and 9 in Fig. 1(c)) contained the same amount of BP as in sample 4, whereas the concentration in sample 5 was higher than these so the loadings were coherent with the experimental knowledge.

PARAFAC decompositions provide a unique chromatographic profile for every compound that is common to all the samples, whereas PARAFAC2 decompositions provide a chromatographic profile of each compound for each sample as can be seen in Fig. 1(a).

According to [34], the tolerance intervals for the relative retention time (the ratio of the chromatographic retention time of the analyte to that of the internal standard) were estimated. The retention times of BHT, DiBP-d_4, DiBP and DEHA obtained through the chromatographic profile of the corresponding PARAFAC model are collected in the second column of Table 2A. It was not possible to establish a retention time for DiNP since this analyte has a finger-peak chromatographic signal. In the case of BP, the median of the retention times obtained for this analyte in the PARAFAC2 decomposition was used to estimate this tolerance interval. It was checked that all the relative retention times obtained from the chromatographic profile of BP for each sample were within the tolerance interval built with a tolerance margin of ±0.5% as [34] states.

On the other hand, PARAFAC and PARAFAC2 decompositions provide a unique spectral profile for each analyte that is common to all the samples. So, the spectral loadings obtained in these decompositions were used to calculate the relative ion abundances of each *m/z* ratio with regard to the loading of the base peak and thus determine the permitted tolerance intervals according to [34].

The unequivocal identification of the analytes in the following stages of this work was carried out considering the tolerance intervals for the relative retention time and for the relative ion abundances as reference, which are listed in column 4 of Table 2A and column 5 of Table 2B, respectively.

In this work, all the analytes were unequivocally identified according to regulations [34,35,36]. In addition, the GC/MS system remained remarkably stable over time since the values of the relative retention times and the relative ion abundances obtained in a previous work of the authors [39] were within the tolerance intervals of this work.

4.2. Migration from different food contact materials into Tenax

Five types of food contact materials were studied to determine the migration of the analytes considered in this work into Tenax as food simulant. Three of these food packaging materials were made of plastic (PE and PVC cling-films for wrapping foodstuffs and PP coffee capsules), whereas the rest were made of paper (brown paper popcorn bag intended to be heated in a microwave oven and paper bread bag). Five non-spiked and other five spiked migration samples were prepared and analysed for each of those food contact materials. The whole migration test procedure in each case and the extraction procedure are detailed in Sections 2.4.2 and 2.4.3, respectively. Two Tenax blanks were also prepared following those procedures for each type of food contact material but in this case Tenax was not into contact with the material to check if the analytes were already present in the Tenax. The migration test conditions (test time and temperature) were chosen according to Commission Regulation (EU) 2016/1416 [19] considering the worst foreseeable conditions of use of the corresponding material. In the case of the PP coffee capsules, two migration tests were conducted: one of them at 100ºC for 5 min since these are the worst foreseeable conditions of use according to [19], and the other one was performed under severe conditions of use (100ºC for 10 days, see Section 2.4.2). Nine solvent calibration standards were prepared for each analyte. The total ion chromatogram (TIC) shown in Fig. 2(a) was obtained from the injection of the solvent calibration standard at the highest concentration during the analysis of the PP coffee capsules. Fig. 2(b) also shows the chromatogram related to a Tenax blank measured during that analysis, whereas

Fig. 2(c) is the chromatogram of a non-spiked migration sample of the PP coffee capsules carried out at 100ºC for 5 min. Only a peak for BP seemed to appear in Fig. 2 (c). A calibration based on a PARAFAC decomposition was performed. The calibration line for BP in this case was $y = -8.18 \cdot 10^{-2} + 1.08 \cdot 10^{-2}\, x + 2.97 \cdot 10^{-4}\, x^2$ ($R^2 = 99.72\%$, $s_{yx} = 8.76 \cdot 10^{-2}$), whereas the accuracy line for this analyte was $y = 4.00 \cdot 10^{-1} + 0.99\, x$ ($R^2 = 98.77\%$, $s_{yx} = 4.23$). The method had not proportional or constant bias. The values of CCα and CCβ with the probabilities of false positive (α) and false negative (β) fixed at 0.05 were 9.02 and 17.49 μg L^{-1}, respectively. The average amount found of BP in those non-spiked migration samples was above CCα but below CCβ. Therefore, none of the analytes were detected in the migration test of the PP coffee capsules performed at 100ºC for 5 min. However, the migration test for these capsules were performed under severe conditions and the results obtained in that case will be discussed throughout this section.

To carry out the quantification of the amount migrated in each case, nine solvent calibration standards were prepared for each food contact material within the concentration ranges of every analyte listed in Table 1 (columns 8-13) since the analysis of each material was performed in different days. In all cases, the lowest concentration of DiBP in the calibration standards was 25 μg L^{-1} since the ubiquity of DiBP by a non-constant leaching process was detected in a previous work [48] and that amount was proved to be statistically greater than the one considered as blank in our laboratory (α = β = 0.012). A solvent blank and seven system blanks were also measured throughout each analysis to control the cleanliness of the GC/MS system.

In addition, four control samples were injected throughout the analytical sequence in the analysis of each material for the assessment of the performance of the GC/MS equipment. These samples were solvent standards containing 50 μg L^{-1} of BHT, BP, DiBP and DEHA, 2 mg L^{-1} of DiNP and 25 μg L^{-1} of DiBP-d_4.

The migration samples prepared with the first food contact material analysed in this work (PE cling-film) and the four control samples of that analysis were stored in the refrigerator at 4ºC for five days until their measurement to check the stability of the analytes. These samples together with other four newly prepared control samples and the calibration standards were analysed the same day.

After GC/MS analyses, the samples measured for the analysis of each food contact material (see columns 2-7 of Table 1) were arranged in three-way arrays and PARAFAC decompositions (or PARAFAC2 decompositions in the case of BP) were performed. Table S1 of the Supplementary Material collects the dimensions of each three-way array together with some features of the model estimated in each case.

The abundance of DiBP-d_4 is much lower than the abundance of DiBP at the studied concentrations and the peaks of both compounds are completely overlapped. Therefore, some additional solvent standards were added to the three-way array of DiBP and DiBP-d_4 to obtain an adequate PARAFAC model since PARAFAC needs a greater variation of DiBP-d_4. A standard containing all the analytes (25 μg L^{-1} of BHT and BP, 50 μg L^{-1} of DiBP and DEHA and 2 mg L^{-1} of DiNP) and a higher amount of DiBP-d_4 (100 μg L^{-1}) was added to the three-way array for the analysis of the PE film and the popcorn bag. In the analysis of the bread bag, that sample was added together with another standard only containing 100 μg L^{-1} of DiBP-d_4. Two standards were also included in the three-way array for the PP coffee capsules: one of them containing the analytes at those same concentrations mentioned above and DiBP-d_4 at 75 μg L^{-1} and the other only containing 100 μg L^{-1} of DiBP-d_4.

One of the non-spiked migration samples obtained from the PVC film exceeded the threshold value of the Q and Hotelling's T^2 statistics at the 95% confidence level in the PARAFAC model for DEHA so it was

considered an outlier and removed from that three-way array. Then, the PARAFAC model was estimated again without that sample (see Table S1 of the Supplementary Material).

The correction of the baseline in the chromatograms of the samples contained in the three-way arrays for the analysis of the PP coffee capsules (under severe conditions) was not performed since a lot of peaks appeared in the chromatograms of the non-spiked and spiked migration samples. Fig. 2(d) shows an example of one of these chromatograms. An unidentified interferent present in these migration samples appeared in the PARAFAC models for all the analytes. The baseline appeared as another factor in these models for BP, DEHA and DiNP. In the case of BP, only 24 scans instead of the 49 scans were only considered to minimize the effect of an interferent that made difficult the extraction of the factor related to BP (see Table S1 of the Supplementary Material). An unidentified interferent also appeared in the PARAFAC2 model for BP in the analysis of the paper bread bag.

By way of example, the loadings of the three-factor PARAFAC model estimated from the common three-way array for DiBP and DiBP-d_4 in the analysis of the PP coffee capsules (under severe conditions) are shown in Fig. 3. The abundance between both compounds is clearly different in Fig. 3 (a), as already mentioned. The third factor of this model was related to an interferent together with the baseline. All the *m/z* ratios recorded for DiBP and DiBP-d_4 were shared with this factor as can be seen in Fig. 3(b). PARAFAC has solved this coelution problem as can be seen in that figure. The sample loadings (see Fig. 3(c)) for this third factor were low and remained constant except for the migration samples where the loadings were high. The loadings of the sample profile for DiBP and DiBP-d_4 were zero in the solvent and system blanks, whereas the sample loadings for DiBP increased with the concentration of the solvent calibration standards as expected. In addition, an amount of DiBP seemed to be present in the non-spiked migration samples (see Fig. 3(c) in blue). The control samples measured in this analysis correspond to samples number 3, 14, 24 and 32. This PARAFAC sample profile was coherent with the known concentration even in the two additional samples added to this three-way array (samples 34 and 35).

The last column of Table S1 of the Supplementary Material shows that a two-factor PARAFAC model was needed for DiNP in all cases except for the analysis of the migration from the PP coffee capsules (under severe conditions). The baseline appeared as a factor in all these models. The chromatographic, spectral and sample loadings of the three-factor PARAFAC model for DiNP in the analysis of the PP capsules can be seen in Fig. 4. This is a special case since the chromatographic signal of DiNP is complex and appears as finger peaks due to an array of possible C_9 isomers (see Fig. 2(a) and Fig. 4(a)). As can be seen in Fig. 4(b), the *m/z* ratio 57 was characteristic of the baseline, whereas the most characteristic *m/z* ratios for the interferent were 57 and 127 which were shared with DiNP. The sample loadings for DiNP (see Fig. 4(c)) increased with the concentration of the solvent calibration samples, whereas they were zero for the solvent blank, system blanks, Tenax blanks and non-spiked migration samples. Therefore, DiNP was not contained in the Tenax used in the analysis and it did not migrate from the PP coffee capsules. Samples number 3, 14, 24 and 32 were the control samples as in Fig. 3(c). The sample loadings for the baseline remained constant except for the system blanks in which these loadings were lower. On the other hand, the interferent that coeluted with DiNP came from the PP coffee capsules since the sample loadings of this interferent were zero for all the samples except for the migration samples (see Fig. 4(c)). This interferent, that clearly appeared in the chromatograms of the migration samples as can be seen in Fig. 2(d), has been separated perfectly from the analyte in this model.

Although many peaks appeared in the TICs of the migration samples in the analysis of the PP coffee capsules (under severe conditions), it is clear from Fig. 3(c) and Fig. 4(c) that none of these compounds remained in the GC/MS system after the measurement of these samples since the sample loading for the

analytes and for the interferents in the system blank injected after the migration samples (sample number 31) was zero.

The relative retention times of all the analytes obtained through the chromatographic profile (see Table 2A, columns 5-9) and the relative abundances of each diagnostic ion calculated with the spectral profile (see Table 2B, columns 6-10) in the analysis of the five food contact materials lay within the corresponding tolerance intervals established previously in Section 4.1 (column 4 of Table 2A and column 5 of Table 2B). Only the relative abundance of *m/z* ratio 51 for BP and *m/z* ratio 209 for DiBP-d_4 in the analysis of the PP coffee capsules (under severe conditions) lay outside their corresponding tolerance interval. However, the analytes were unequivocally identified in all cases since at least 3 *m/z* ratios for each analyte met the identification conditions.

The sample loadings of each analyte obtained in the analysis of each food contact material were standardized with the ones of DiBP-d_4 of the corresponding model in each case. The sample loadings for BP were normalized prior to standardization in all cases since they came from a PARAFAC2 model. Next, calibration models "standardized sample loading versus true concentration" were fitted and validated for each analyte in each analysis with the nine standards. Table S2 of the Supplementary Material collects the parameters of these regression models together with the number of outliers which had been removed in each case to perform the regression model since they had a studentized residual greater than 3 in absolute value. These regression models were significant in all cases. The mean of the absolute value of the relative errors in calibration ranged from 1.40% (n=8) to 8.77% (n=4) in the whole study when the samples with predicted concentration lower than the corresponding CCβ had been excluded. Table S2 of the Supplementary Material also includes the parameters of the accuracy lines related to the calibration models performed for each analyte in each case, that is, the regressions "predicted concentration versus true concentration". The intercept and the slope of these accuracy lines were significantly equal to 0 and 1, respectively, at a 95% confidence level so the property of trueness was fulfilled for all the analytes in all cases. The values of CCα and CCβ with the probabilities of false positive (α) and false negative (β) fixed at 0.05 are listed in Table 3 (columns 3 and 4) for all the analytes in each analysis.

The concentration of every analyte in the control samples measured in each analysis was determined from the corresponding calibration model. The values of the average predicted concentration and the coefficient of variation obtained in each case for these samples are given in the two last columns of Table 3. An outlier was removed in the estimation of DEHA in the analysis of the PVC film. The lowest values of the coefficient of variation were obtained for DiBP as can be seen in Table 3. There was no problem in the performance of the GC/MS equipment at the sight of the values obtained for the control samples.

The stability study carried out during the analysis of the PE film revealed from the comparison between the two types of control samples measured that DEHA is not stable over time as can be seen in the average predicted concentration of those samples in Table 3. Therefore, it could be concluded that the extracts should not be stored before their injection in the GC/MS system.

Table 4 contains the values of the average concentration found of every analyte in the Tenax blanks and in the non-spiked migration samples in each case. As can be seen in this table, BP and DiNP was not detected in the Tenax since the average concentrations were below their corresponding CCβ values. There was an amount of DiBP in the Tenax measured for the analysis of the PE and PVC films and of the popcorn bag. DEHA was only present in the Tenax measured for the analysis of the PP coffee capsules (under severe conditions), whereas Tenax contained BHT in all the analyses.

The migration of some of the analytes was only detected in the PVC film and in the coffee capsules (under severe conditions, see Table 4). The average concentrations found in the rest of the cases were below the corresponding CCβ values. The amount of BP, DiBP and DEHA migrated from the PVC film was 71.25 µg L^{-1}, 19.04 µg L^{-1} and 268 µg L^{-1}, respectively. In the case of DiBP, the concentration found in two non-spiked samples of the PVC film was below the corresponding CCβ, so these samples were not considered in the estimation. The average concentration found of DEHA in the PVC film was calculated with the four non-spiked samples considered in the three-way array for this analyte in this case. On the other hand, the amount of BP and DiBP migrated from the PP coffee capsules (under severe conditions) was 46.45 µg L^{-1} and 13.11 µg L^{-1}, respectively.

4.2.1. Adsorption capability of Tenax

The behaviour of Tenax as a food simulant in the analysis of the migration of the analytes of this work was also studied. The adsorption capability of Tenax as food simulant was expressed as the percentage of the quantity of each analyte initially added to every spiked migration sample that has migrated to Tenax at last in each case. Table 5 contains the average values of the adsorption capability of Tenax together with the corresponding coefficient of variation for every analyte in each analysis. The average adsorption capability ranged from 25.33% to 99.37%, being the best value one of BP (whose values ranged from 64.85% to 99.37%). The values corresponding to BHT in the analysis of the bread bag and the ones for DEHA in the analysis of the PE and PVC films were not calculated since the predicted concentration of the amount added to the spiked migration samples was below their CCβ. In addition, the values of the coefficient of variation were high in many of the cases. These results may depend on the analyte and on the nature of the packaging material and its contact with the Tenax since the contact between Tenax and the material is not uniform in some cases. The corresponding correction factor (using the values of the adsorption capability of Tenax contained in Table 5) has been applied to the amounts of BP and DiBP migrated from the PVC film and from the PP coffee capsules (see Section 4.2). Therefore, the real amount of BP and DiBP migrated from the PVC film was 83.53 µg L^{-1} and 31.30 µg L^{-1}, respectively; whereas 71.62 µg L^{-1} of BP and 27.45 µg L^{-1} of DiBP migrated from the PP coffee capsules under severe conditions. Obviously, this correction is not applied when the chromatographic procedure does not enable the quantification, that is, when the values are below CCβ.

It must be taken into account that Tenax is an expensive simulant and its reuse in this multiresidue analysis is not possible as a previous work stated [39]. In addition, this simulant is difficult to manage since it is a fine and light powder prone to static electricity which gets stuck to the food contact material. All these facts make difficult the performance of the migration test using Tenax.

The low values of adsorption capability and the variability obtained in some cases (see Table 5) may question the use of Tenax as an adequate food simulant for testing the migration of these analytes into dry foodstuffs. In addition, several works [13,14,15] have also had difficulties in the use of Tenax as a food simulant as commented in the Introduction section and it may not be representative of the real migration into foodstuffs. Therefore, a coordinated global effort should be made to tackle this problem in the near future.

5. Conclusions

PARAFAC and PARAFAC2 decompositions have enabled the unequivocal identification and quantification of all the analytes according to the requirements established by regulations currently in force despite some of the *m/z* ratios of the coeluting interferents were shared with the analytes. In addition, PARAFAC has dealt with finger-peak chromatographic signals such as that of DiNP.

The suitability of Tenax as a food simulant in the analysis of the migration of the analytes of this work from five different food contact materials has been questioned considering the values of the adsorption capability obtained.

The stability study carried out during the analysis of the PE film revealed that DEHA is not stable over time, so the extracts should not be stored before their injection in the GC/MS system.

The presence of BHT, DiBP and DEHA has been confirmed in the Tenax blanks in some of the analyses. In addition, BP, DiBP and DEHA have migrated from the PVC film; whereas the migration of BP and DiBP from PP coffee capsules has also been confirmed.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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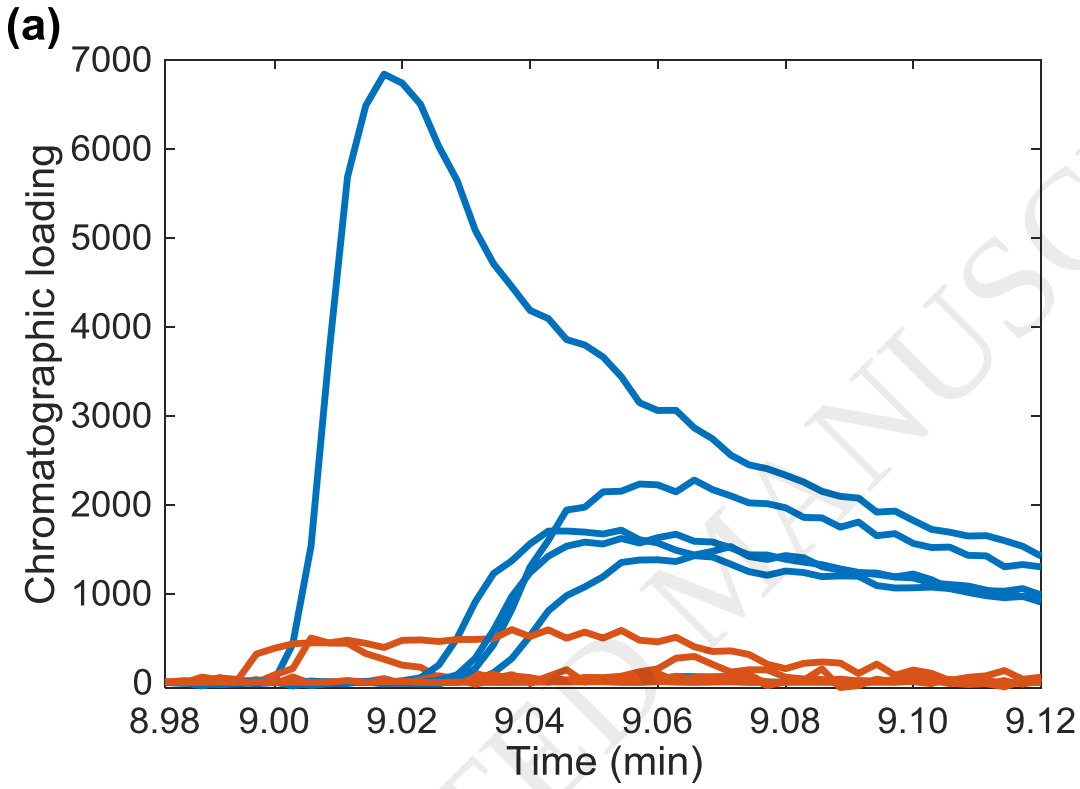
FIGURE CAPTIONS

Fig. 1 PARAFAC2 model with two factors obtained with the three-way array that contained the reference samples for BP (blue: BP, orange: interferent). Loadings of the: (a) chromatographic profile, (b) spectral profile and (c) sample profile. Samples 1, 6 and 10: system blanks, sample 2: solvent blank without IS, samples 3, 4 and 5: reference standards containing BP at three concentration levels, and samples 7, 8 and 9: reference standards containing BP at the same amount as in sample 4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).



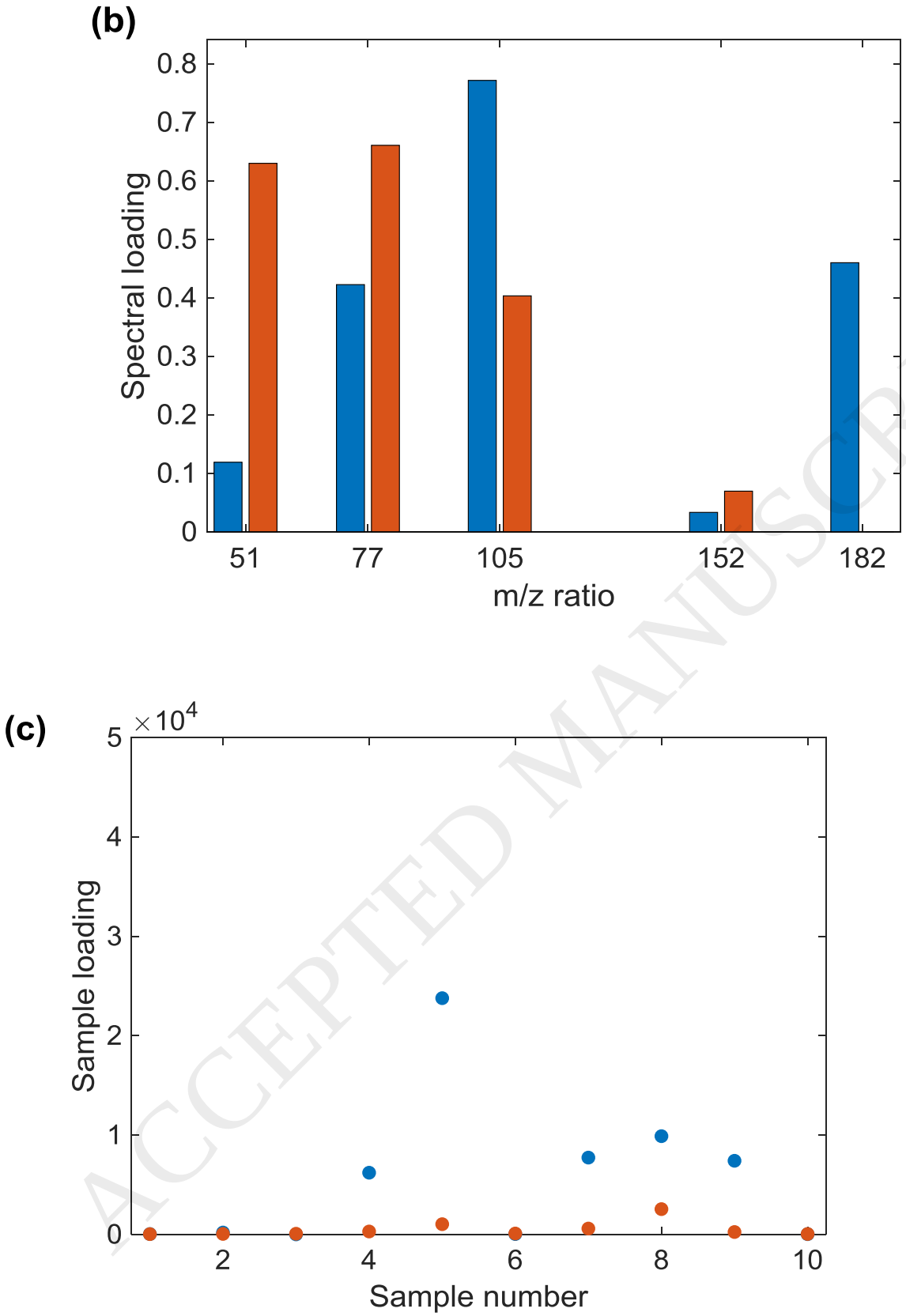
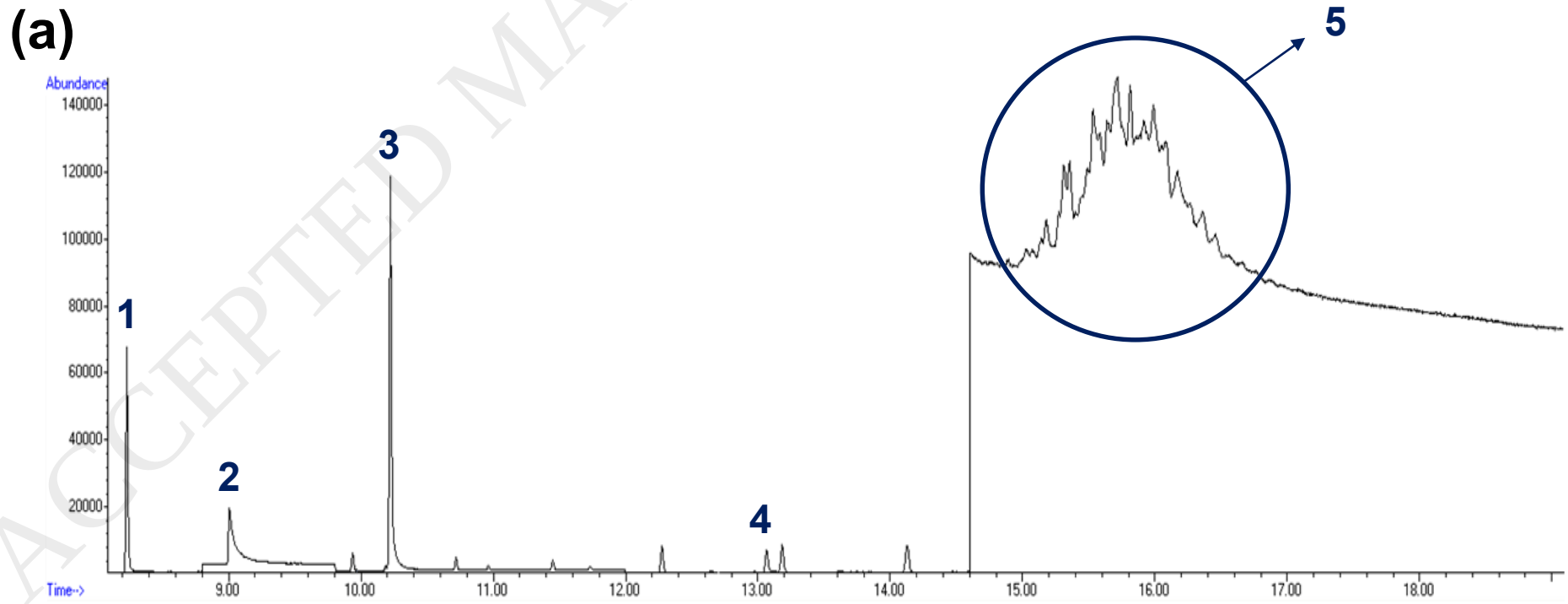
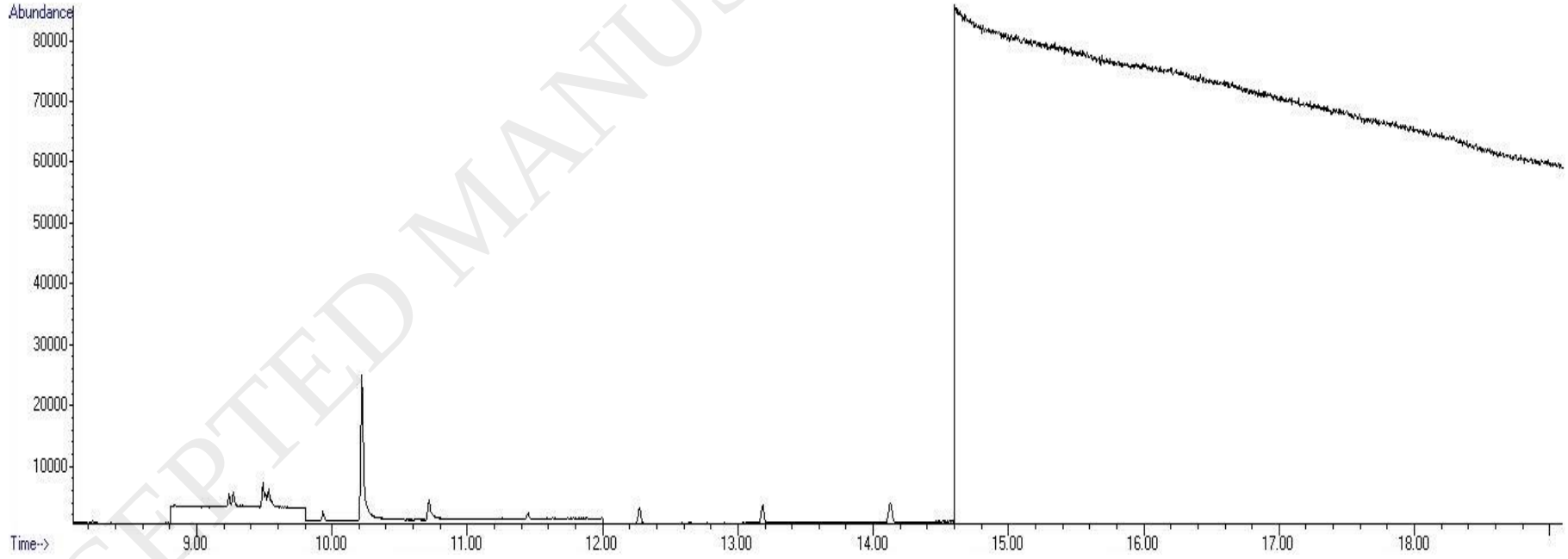


Fig. 1

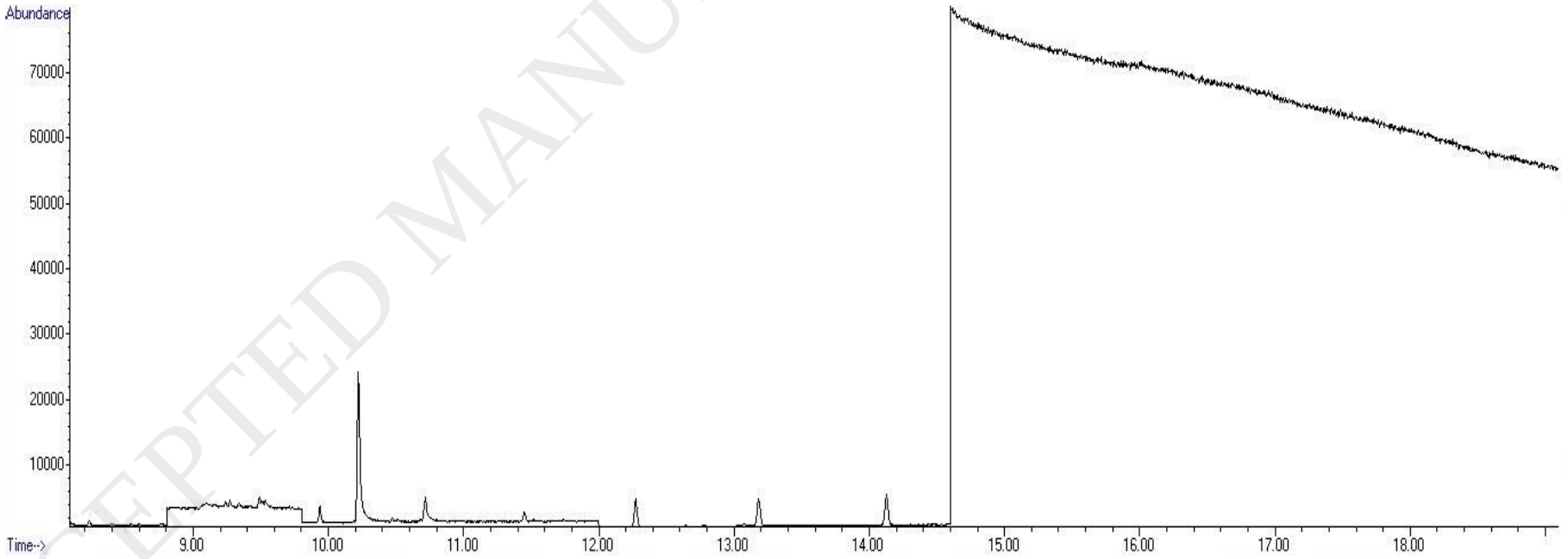
Fig. 2 Total ion chromatograms (TICs) obtained from the injection of: (a) a solvent calibration standard containing 100 µg L^{-1} of BHT, BP and DEHA, 130 µg L^{-1} of DiBP, 25 µg L^{-1} of DiBP-d_4 and 4000 µg L^{-1} of DiNP prepared during the analysis of the PP coffee capsules, (b) a Tenax blank measured during the analysis of the migration from the PP coffee capsules at 100ºC for 5 min, (c) an extract obtained after the migration test of a PP coffee capsule performed at 100ºC for 5 min and ~~(b)~~ (d) an extract obtained after the migration test (under severe conditions) of a coffee capsule made of polypropylene. Peak labels: 1, BHT; 2, BP; 3, DiBP and DiBP-d_4; 4, DEHA; 5, DiNP.



(b)



(c)



(d)

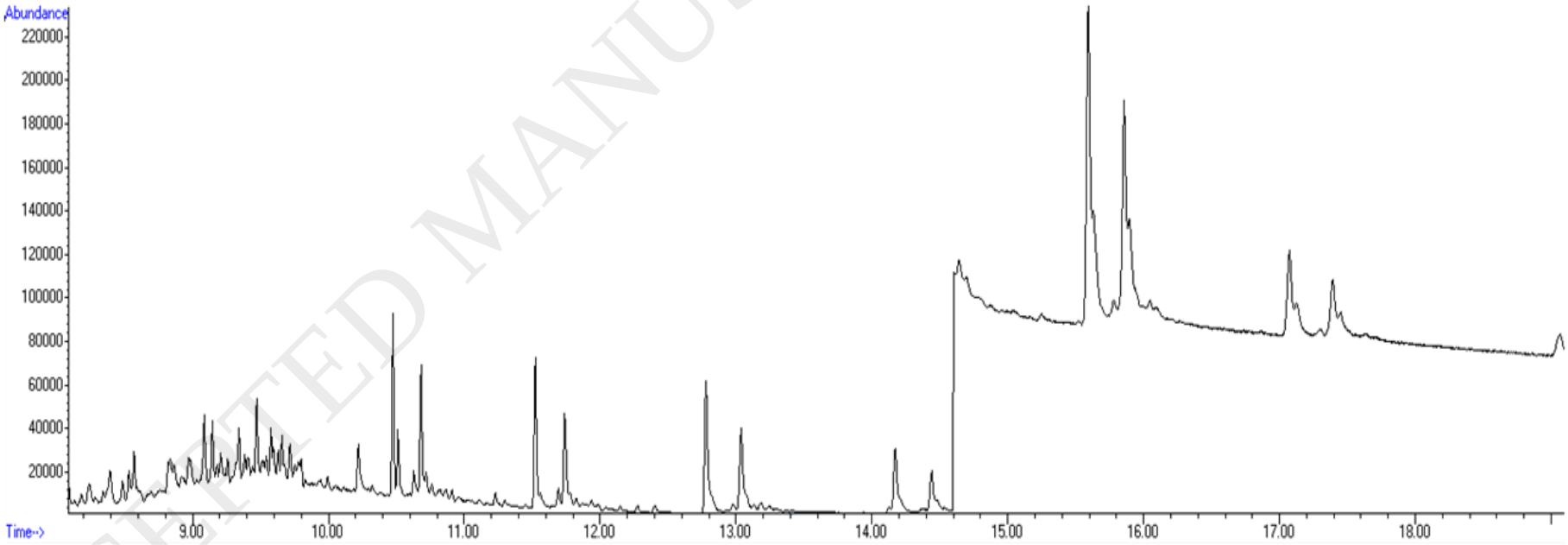
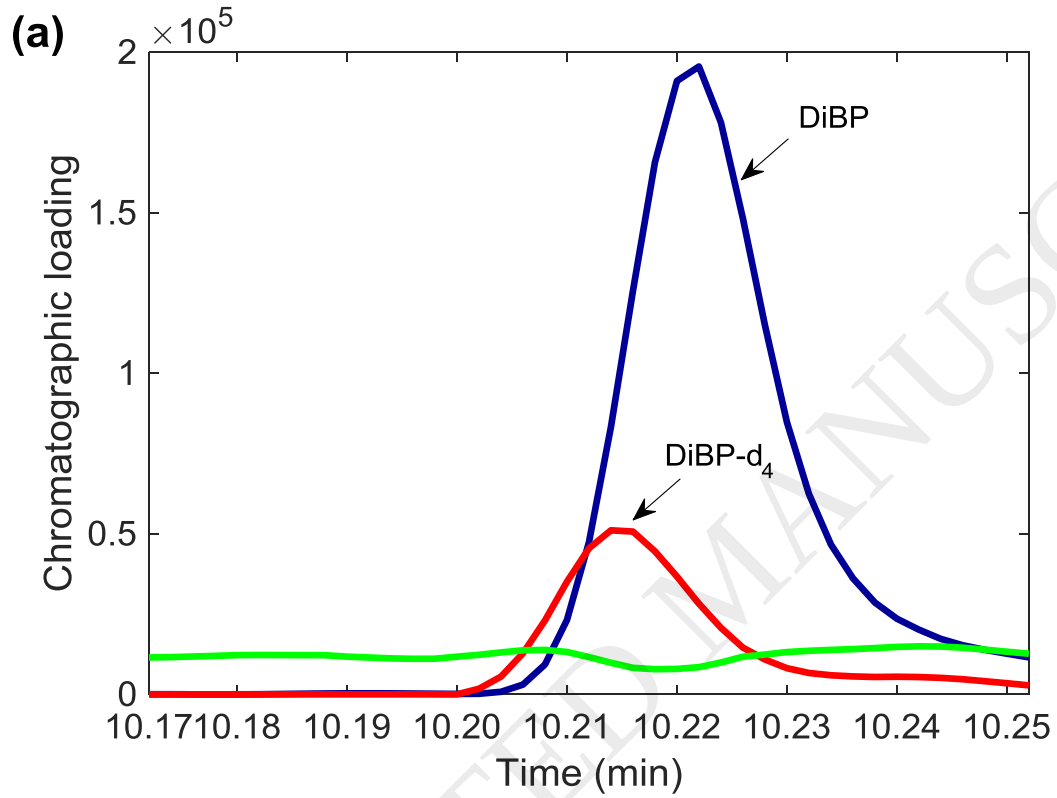
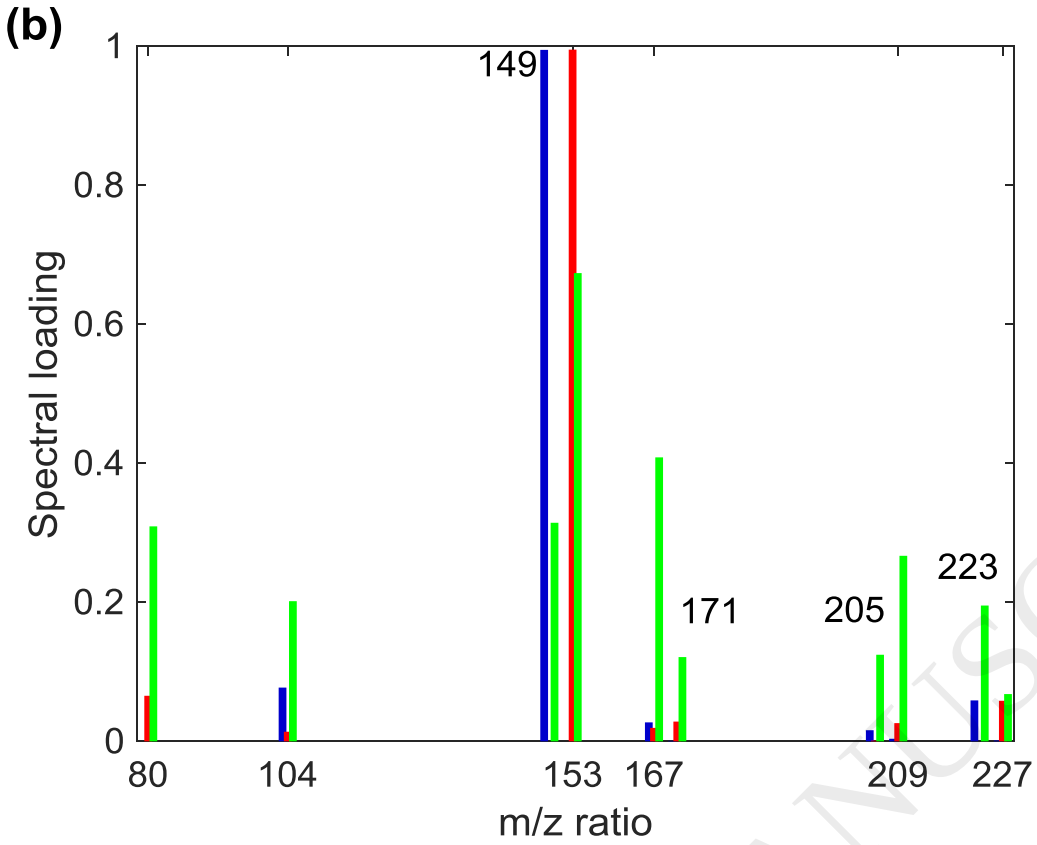


Fig. 2

Fig. 3 Loadings of the (a) chromatographic, (b) spectral and (c) sample profiles of the three-factor PARAFAC model fitted with the common three-way array for DiBP and DiBP-d_4 that contained the data corresponded to the analysis of the migration from a PP coffee capsule (under severe conditions). Factor 1 (DiBP) is in dark blue, factor 2 (DiBP-d_4) is in red, while the interferent is in light green. Samples number 3, 14, 24 and 32 (control samples) are indicated in Fig. 3(c) for an easier understanding of the text. Samples 34 and 35: additional samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).





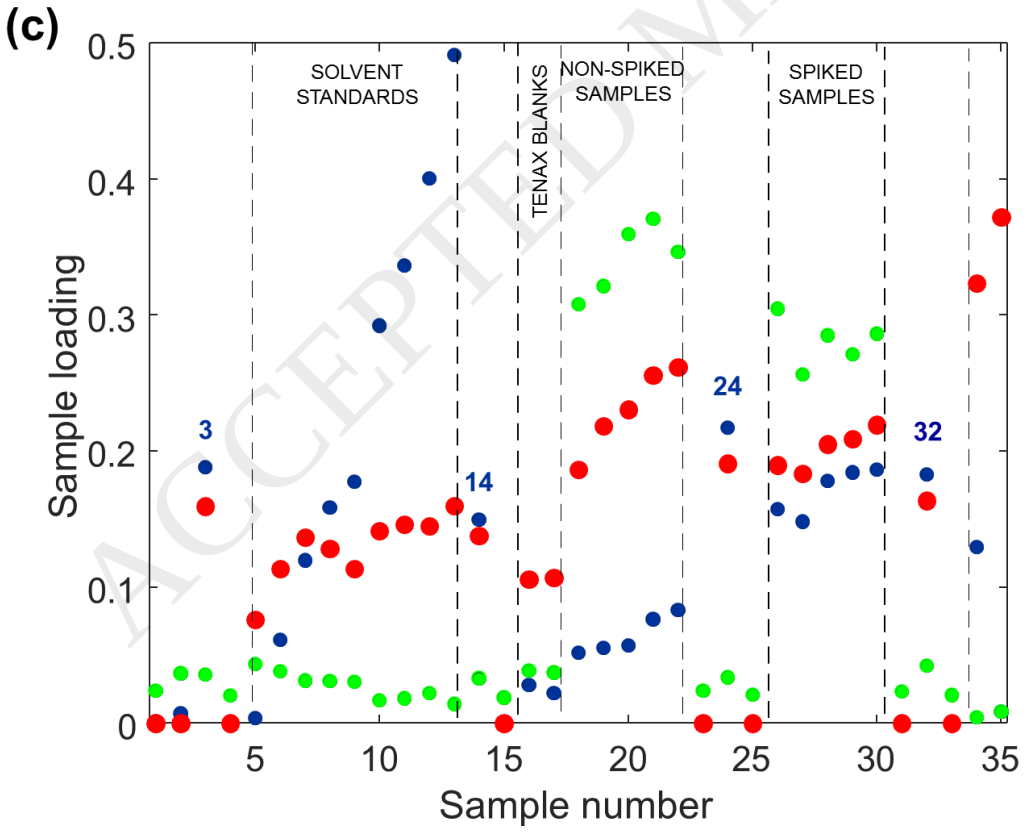
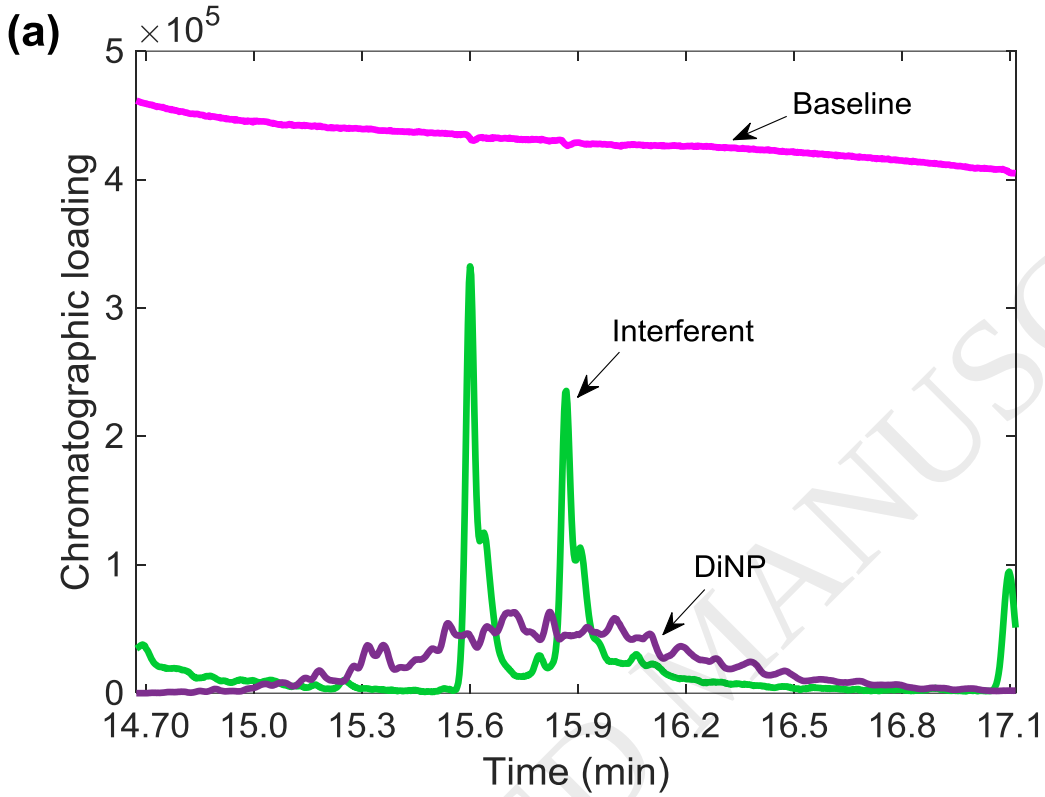
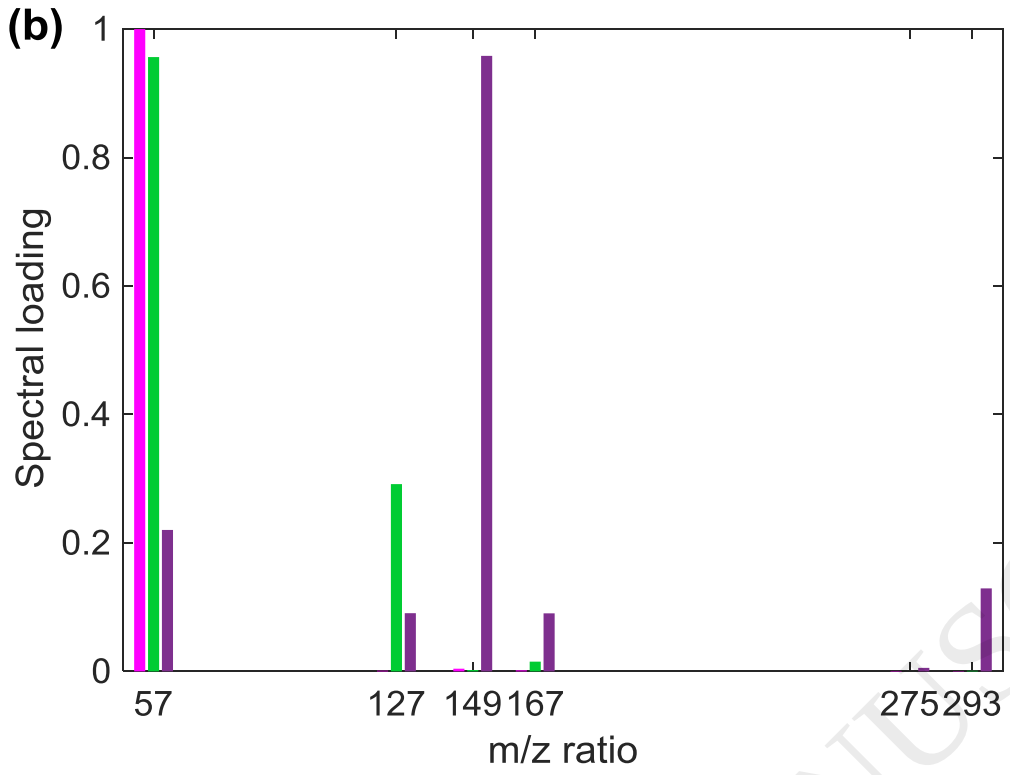


Fig. 3

Fig. 4 PARAFAC model with three factors obtained with the three-way array of DiNP built for the analysis of the migration from a PP coffee capsule (under severe conditions). Loadings of the: (a) chromatographic profile, (b) spectral profile and (c) sample profile. Factor 1 (baseline) is in pink, factor 2 (interferent) is in green, while factor 3 (DiNP) is in purple. Samples number 3, 14, 24 and 32 (control samples) are indicated in Fig. 4(c) for an easier understanding of the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).





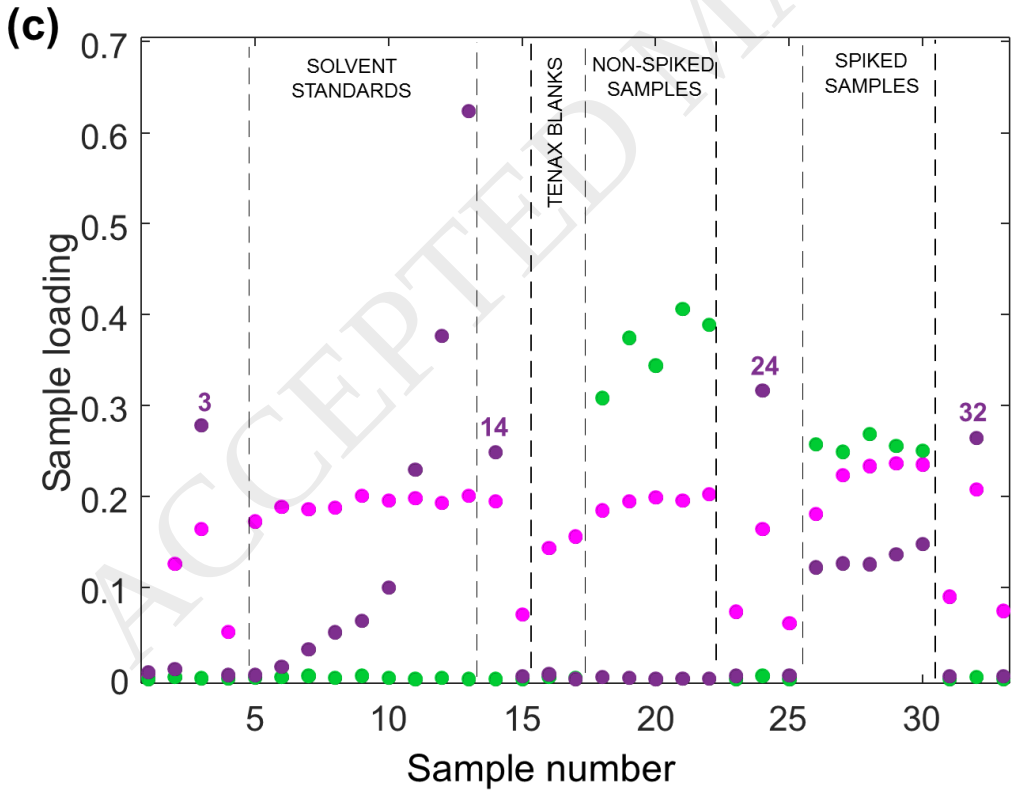


Fig. 4

Table 1 Summary of the samples analysed and of the concentration ranges for every analyte in each experimental stage of this work.

Analytical stage	Number of samples analysed						Concentration range (μg L^{-1})					
	a	b	c	d	e	f	BHT	BP	DiBP-d_4	DiBP	DEHA	DiNP
Tolerance intervals [g]	3	1	6	-	-	-	0-100	0-100	0-100	0-125	0-125	0-5000
Migration from PE film	7	1	17	2	5	5	0-100	0-100	25	0-130	0-100	0-4000
Migration from paper bread bag	7	1	13	2	5	5	0-100	0-100	25	0-130	0-100	0-4000
Migration from PVC film	7	1	13	2	5	5	0-100	0-150	25	0-130	0-500	0-4000
Migration from brown paper popcorn bag	7	1	13	2	5	5	0-100	0-100	25	0-130	0-100	0-4000
Migration from PP coffee capsules (severe conditions)	7	1	13	2	5	5	0-100	0-100	25	0-130	0-100	0-4000

a: system blanks, b: solvent blank without IS, c: solvent standards, d: Tenax blanks, e: non-spiked migration samples, f: spiked migration samples (for the evaluation of the adsorption capability of Tenax).

[g] For the relative retention time and for the relative ion abundances.

Table 2 Tolerance intervals for: A) the relative retention time and for B) the relative ion abundances estimated from the loadings of the chromatographic and spectral profiles, respectively. It is not possible to establish a retention time for DiNP. Identification of every analyte in the migration tests performed. In bold, the relative abundance of the *m/z* ratio which is not within its corresponding tolerance interval.

A) Retention time

Analyte	t_R (min)	Relative t_R	Tolerance interval	Identification (relative retention time)				
				PE film	Bread bag	PVC film	Popcorn bag	PP capsules
BHT	8.232	0.806	(0.802-0.810)	0.806	0.806	0.806	0.806	0.806
BP	9.052	0.886	(0.882-0.890)	0.887	0.885	0.882	0.885	0.884
DiBP-d_4	10.217	1.000	(0.995-1.005)	1.000	1.000	1.000	1.000	1.000
DiBP	10.226	1.001	(0.996-1.006)	1.001	1.001	1.001	1.001	1.001
DEHA	13.069	1.279	(1.273-1.286)	1.279	1.279	1.279	1.279	1.279

B) Diagnostic ions

Analyte	*m/z* ratio	Spectral loading	Relative abundance (%)	Tolerance interval (%)	Identification (relative abundances for each diagnostic ion, %)				
					PE film	Bread bag	PVC film	Popcorn bag	PP capsules
BHT	91	$6.54 \cdot 10^{-2}$	6.80	(3.40-10.20)	6.68	6.55	6.53	6.64	6.47
	145	$1.14 \cdot 10^{-1}$	11.85	(9.48-14.22)	11.70	11.61	11.53	11.68	12.05
	177	$7.28 \cdot 10^{-2}$	7.57	(3.79-11.36)	7.64	7.59	7.54	7.62	8.12
	205[a]	$9.62 \cdot 10^{-1}$	100	-	100	100	100	100	100
	220	$2.29 \cdot 10^{-1}$	23.83	(20.26-27.41)	24.00	24.13	24.06	24.05	24.62
BP	51	$1.19 \cdot 10^{-1}$	15.40	(12.32-18.48)	16.81	14.80	17.07	16.37	**24.68**
	77	$4.22 \cdot 10^{-1}$	54.76	(49.28-60.24)	59.02	55.61	56.26	56.03	52.96
	105[a]	$7.71 \cdot 10^{-1}$	100	-	100	100	100	100	100
	152	$3.31 \cdot 10^{-2}$	4.29	(2.15-6.44)	4.65	4.33	4.27	4.40	4.54
	182	$4.60 \cdot 10^{-1}$	59.61	(53.65-65.57)	62.69	59.06	58.38	59.27	55.43
DiBP-d_4	80	$5.74 \cdot 10^{-2}$	5.76	(2.88-8.64)	5.95	5.96	5.70	5.82	6.58
	153[a]	$9.97 \cdot 10^{-1}$	100	-	100	100	100	100	100
	171	$2.61 \cdot 10^{-2}$	2.62	(1.31-3.93)	2.56	2.71	2.51	2.64	2.85
	209	$1.33 \cdot 10^{-2}$	1.33	(0.67-2.00)	1.25	1.40	1.49	1.31	**2.63**
	227	$4.92 \cdot 10^{-2}$	4.94	(2.47-7.47)	5.05	5.09	5.19	5.17	5.86
DiBP	104	$8.04 \cdot 10^{-2}$	8.08	(4.04-12.12)	7.78	7.87	7.71	7.67	7.77
	149[a]	$9.95 \cdot 10^{-1}$	100	-	100	100	100	100	100
	167	$2.75 \cdot 10^{-2}$	2.76	(1.38-4.14)	2.77	2.77	2.80	2.79	2.73
	205	$1.33 \cdot 10^{-2}$	1.34	(0.67-2.01)	1.39	1.40	1.43	1.44	1.61
	223	$5.25 \cdot 10^{-2}$	5.28	(2.64-7.92)	5.44	5.49	5.66	5.55	5.92
DEHA	112	$3.10 \cdot 10^{-1}$	33.02	(28.07-37.97)	34.21	34.73	31.31	32.29	35.31
	129[a]	$9.38 \cdot 10^{-1}$	100	-	100	100	100	100	100
	147	$1.50 \cdot 10^{-1}$	16.03	(12.82-19.24)	16.25	16.01	16.50	16.43	17.29
	241	$3.99 \cdot 10^{-2}$	4.25	(2.13-6.38)	4.16	4.31	4.48	4.45	4.92
	259	$1.60 \cdot 10^{-2}$	1.71	(0.86-2.57)	1.84	1.76	2.00	1.91	2.29
DiNP	57	$2.49 \cdot 10^{-1}$	26.11	(22.19-30.03)	24.86	26.59	26.71	25.27	22.98
	127	$9.06 \cdot 10^{-2}$	9.51	(4.76-14.27)	9.46	9.53	9.73	9.47	9.45
	149[a]	$9.53 \cdot 10^{-1}$	100	-	100	100	1100	100	100
	167	$8.91 \cdot 10^{-2}$	9.35	(4.68-14.03)	9.43	9.42	9.45	9.66	9.43
	275	$5.50 \cdot 10^{-3}$	0.58	(0.29-0.87)	0.59	0.58	0.61	0.60	0.57
	293	$1.18 \cdot 10^{-1}$	12.43	(9.94-14.92)	12.65	12.71	13.02	13.16	13.48

The values of the relative retention time for BP were calculated with the median of the retention times obtained for BP in the corresponding PARAFAC2 decomposition.

[a] Base peak.

Table 3 Decision limit (CCα) and capability of detection (CCβ) at $x_0 = 0$ ($\alpha = \beta = 0.05$) for each analyte and analysis. Added concentration of every analyte in the control samples together with the values of the average predicted concentration (C_{pred}) and the coefficient of variation obtained for these samples in each case.

Analyte	Migration test	CCα (µg L^{-1})	CCβ (µg L^{-1})	Control samples (n=4)			
				Added concentration (µg L^{-1})	Average C_{pred} (µg L^{-1})	Coefficient of variation (%)	
BHT	PE film	1.80	3.48	50	62.71[a]	60.27[b]	11.06[a]	9.33[b]
	Bread bag	3.17	6.13		52.57		5.38	
	PVC film	5.88	11.34		44.78		13.08	
	Popcorn bag	2.14	4.14		53.02		12.84	
	PP coffee capsules[c]	3.93	7.62		54.43		3.60	
BP	PE film	11.63	22.56	50	57.08[a]	57.11[b]	3.53[a]	1.80[b]
	Bread bag	6.31	12.24		58.89		3.63	
	PVC film	7.41	14.36		54.99		8.15	
	Popcorn bag	7.33	14.21		56.28		4.14	
	PP coffee capsules[c]	12.63	24.49		57.61		4.11	
DiBP	PE film	3.97	7.67	50	51.37[a]	54.06[b]	3.47[a]	1.50[b]
	Bread bag	3.70	7.14		48.60		1.51	
	PVC film	5.74	11.13		50.98		1.07	
	Popcorn bag	2.65	5.15		52.45		2.48	
	PP coffee capsules[c]	6.01	11.65		48.92		3.39	
DEHA	PE film	7.96	15.36	50	43.34[a]	56.77[b]	27.34[a]	25.73[b]
	Bread bag	5.07	9.83		50.17		2.25	
	PVC film	22.81	44.37		54.36[d]		9.83[d]	
	Popcorn bag	7.48	14.51		54.23		13.85	
	PP coffee capsules[c]	3.77	7.28		53.65		5.67	
DiNP	PE film	186.58	360.2	2000	2117.81[a]	2216.81[b]	8.04[a]	4.85[b]
	Bread bag	95.25	183.9		2062.65		2.17	
	PVC film	95.55	185.2		2300.81		5.95	
	Popcorn bag	104.42	202.5		2103.86		2.37	
	PP coffee capsules[c]	72.90	141.3		2150.12		3.94	

[a] Control samples stored at 4ºC for five days until their analysis.
[b] Newly prepared control samples the day of the analysis.
[c] Severe conditions.
[d] One outlier has been deleted.

Table 4 Values of the average predicted concentration (C_{pred}) of every analyte in the Tenax blank and in the non-spiked migration samples in each case together with the coefficient of variation obtained for the non-spiked samples.

Analyte	Migration test	C_{pred} Tenax blank (n=2) (µg L^{-1})	Non-spiked migration samples (n=5)	
			Average C_{pred} (µg L^{-1})	Coefficient of variation (%)
BHT	PE film	47.74	< CCβ	-
	Bread bag	15.99	< CCβ	-
	PVC film	21.78	< CCβ	-
	Popcorn bag	10.69	< CCβ	-
	PP coffee capsules [a]	8.58	< CCβ	-
BP	PE film	< CCβ	< CCβ	-
	Bread bag	< CCβ	> CCα and < CCβ	-
	PVC film	< CCβ	71.25	20.13
	Popcorn bag	< CCβ	< CCβ	-
	PP coffee capsules [a]	< CCβ	46.45	3.72
DiBP	PE film	12.35	< CCβ	-
	Bread bag	> CCα and < CCβ	> CCα and < CCβ	-
	PVC film	11.74	19.04 [b]	18.09 [b]
	Popcorn bag	9.59	< CCβ	-
	PP coffee capsules [a]	> CCα and < CCβ	13.11	9.52
DEHA	PE film	< CCβ	< CCβ	-
	Bread bag	> CCα and < CCβ	> CCα and < CCβ	-
	PVC film	< CCβ	268 [c]	7.71
	Popcorn bag	< CCβ	> CCα and < CCβ	-
	PP coffee capsules [a]	8.94	< CCβ	-
DiNP	PE film	< CCβ	< CCβ	-
	Bread bag	< CCβ	< CCβ	-
	PVC film	< CCβ	< CCβ	-
	Popcorn bag	< CCβ	< CCβ	-
	PP coffee capsules [a]	< CCβ	< CCβ	-

[a] Severe conditions.
[b] Only three samples were considered since the concentration of two non-spiked samples was below CCβ.
[c] One of the non-spiked samples was an outlier and had been removed from the three-way array.

Table 5 Average values of the adsorption capability of Tenax (%) for every analyte in the migration tests performed together with the corresponding coefficient of variation.

Analyte	Migration test	Adsorption capability of Tenax (%)	
		Average (%) (n=5)	Coefficient of variation (%)
BHT	PE film	60.65	16.65
	Bread bag	-[a]	-
	PVC film	47.58	24.32
	Popcorn bag	32.16	42.27
	PP coffee capsules [b]	27.35	17.32
BP	PE film	99.37	3.20
	Bread bag	84.65	3.30
	PVC film	85.30	43.01
	Popcorn bag	86.29	6.82
	PP coffee capsules [b]	64.85	3.22
DiBP	PE film	25.33	6.34
	Bread bag	60.25	17.23
	PVC film	60.82	34.51
	Popcorn bag	48.43	5.78
	PP coffee capsules [b]	47.75	5.37
DEHA	PE film	-[a]	-
	Bread bag	56.34	15.56
	PVC film	-[a]	-
	Popcorn bag	92.10	6.68
	PP coffee capsules [b]	55.60	6.84
DiNP	PE film	52.49	13.83
	Bread bag	67.80	2.36
	PVC film	73.06	4.75
	Popcorn bag	43.28	17.11
	PP coffee capsules [b]	47.60	4.09

[a] The predicted concentration of the amount added to the spiked migration samples was below CCβ.
[b] Severe conditions.