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PII: S0039-9140(18)30117-6
DOI: https://doi.org/10.1016/j.talanta.2018.02.011
Reference: TAL18330

To appear in: *Talanta*

Received date: 12 December 2017
Revised date: 1 February 2018
Accepted date: 4 February 2018

Cite this article as: L. Rubio, L.A. Sarabia and M.C. Ortiz, EFFECT OF THE CLEANING PROCEDURE OF TENAX ON ITS REUSE IN THE DETERMINATION OF PLASTICIZERS AFTER MIGRATION BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY, *Talanta,* https://doi.org/10.1016/j.talanta.2018.02.011

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EFFECT OF THE CLEANING PROCEDURE OF TENAX ON ITS REUSE IN THE DETERMINATION OF PLASTICIZERS AFTER MIGRATION BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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Abstract

This paper presents the simultaneous determination of a UV stabilizer (benzophenone (BP)) together with four plasticizers (butylated hydroxytoluene (BHT), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP)) in Tenax by gas chromatography/mass spectrometry and PARAFAC, using DiBP-d_4 as internal standard.

Regulation (EU) No. 10/2011 establishes Tenax as food simulant E for testing specific migration from plastics into dry foodstuffs. This simulant must be cleaned before its use to eliminate impurities. Tenax is expensive, so its reuse would save costs.

A two-way ANOVA was used to study some parameters affecting the cleaning and the extraction of Tenax. The most adequate conditions were chosen taking the values of the coefficient of variation and the average recovery rates of spiked Tenax samples into account.

A study to determine if some analytes remain in Tenax when it is reused and the effect that the cleaning procedure may have in the adsorption capability of Tenax was proposed. This study led to the conclusion that Tenax could not be reused in this multiresidue determination.

All the analytes were unequivocally identified in all the stages of this work and trueness was verified at a 95% confidence level in all cases. A calibration based on PARAFAC provided the following values of capability of detection (CCβ): 2.28 μg L^{-1} for BHT, 10.57 μg L^{-1} for BP, 7.87 μg L^{-1} for DiBP, 3.04 μg L^{-1} for DEHA and 124.8 μg L^{-1} for DiNP, with the probabilities of false positive and false negative fixed at 0.05.

The migration of the analytes from a printed paper sample into Tenax was also studied. The presence of BHT in the food simulant was confirmed and the amount released of this analyte from the paper was 2.56 μg L^{-1}.

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Abbreviations

BP, Benzophenone; BHT, butylated hydroxytoluene; DiBP, diisobutyl phthalate; DEHA, bis(2-ethylhexyl) adipate; DiNP, diisononyl phthalate; CCβ, capability of detection, EURL-FCM, European Reference Laboratory for Food Contact Materials; ILC, interlaboratory comparison; IS, internal standard; SMLs, specific migration limits; RASFF, Rapid Alert System for Food and Feed; EI, electron impact; SIM, single ion monitoring; ANOVA, analysis of variance; CCα, decision limit; CORCONDIA, core consistency diagnostic; LS, linear least squares; α, probability of false positive; β, probability of false negative; $H_{0,}$ null hypothesis; H_a, alternative hypothesis; TIC, total ion chromatogram

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

1. Introduction

The migration of chemicals from food contact materials into food is an important issue in food safety to ensure the protection of human health and the interests of consumers. Food contact materials are all materials and articles intended to come into contact with food such as plastics, paper, ceramic, metals and ink used in food packaging, food containers, etc.

General requirements for all food contact materials are laid down in Framework Regulation (EC) 1935/2004 [1]. The main principle of this Regulation is that any material or article intended to come into contact directly or indirectly with foodstuffs must be sufficiently inert so as not to transfer substances to food in quantities which would: i) endanger human health, ii) bring about an unacceptable change in the composition of the food or iii) bring about a deterioration in the organoleptic properties of the food. The group of materials and articles listed in Annex I of [1] should be manufactured in compliance with the general and detailed rules on good manufacturing practice described in Regulation EC 2023/2006 [2].

However, no food contact material is completely inert, and foodstuffs can be aggressive products that may interact with these materials. Therefore, it is possible that the chemical constituents of food contact materials may migrate into the packaged food [3,4].

Regulation (EU) No 10/2011 [5] establishes poly (2,6-diphenyl-p-phenylene oxide), which is better known under its trade name Tenax®, as food simulant E for testing specific migration from plastics into dry foodstuffs. This regulation also indicates the specifications that must fulfil this simulant: particle size of 60-80 mesh and a pore size of 200 nm. Cereals, sugar, dried or dehydrated fruits and vegetables, milk powder including infant formula, cocoa powder, coffee, spices and seasonings in the natural state such as cinnamon, powdered

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mustard, pepper, vanilla, saffron, salt and dry pasta such as macaroni and spaghetti are examples of dry foodstuffs according to [5].

The European Reference Laboratory for Food Contact Materials (EURL-FCM) has organised several interlaboratory comparison (ILC) exercises related to the identification, migration and quantification of potential migrant substances into food simulant E. In 2012, the EURL-FCM published a report [6] concerning the results of one of the ILCs whose general aim was to evaluate the laboratory performance and precision criteria of the harmonised method for the extraction and quantification of the model substances from Tenax and also for the migration test from a fortified plastic film into this simulant. Then, in 2013, the EURL-FCM performed another ILC [7] about the identification and quantification of unknown substances spiked in Tenax. Regarding the identification of the unknown substances, 48% of the national reference laboratories could identify correctly all the substances, whereas 76% of the laboratories identified correctly all the substances in a follow-up study [8] which reflects the complexity of the analysis.

Tenax is a porous polymer with high adsorption capacity as bulk powder material that efficiently traps volatiles [9,10]. This product presents several advantages such as high thermal stability and high adsorption capacity [10]. In addition, it is reusable many times after its cleaning according to some works [10,11]. However, as far as the authors are aware, there are no studies on the effect that the extensive cleaning of Tenax by Soxhlet may have on its adsorption capability [11,12]. On the other hand, Tenax is expensive [10,11] and difficult to manage [6] since it is a fine and light powder prone to static electricity. The cleaning of Tenax is extremely important since it contains impurities when is sold in bulk, so it must be cleaned prior to its use, even in its first use [9]. Tenax can be cleaned up, for example, by extraction with isooctane [11], diethyl ether [13], etc.; or by Soxhlet extraction using different solvents such as acetone [6,9], diethyl ether [10], acetonitrile [12], methanol and hexane [14].

Apart from plastics, printed paper and board are the most commonly used food packaging materials [15] that can be in contact with food directly or indirectly [16]. These materials are listed in Annex I of the Framework Regulation [1] as a type of material that should be covered by specific harmonized rules. However, they are not currently covered by specific European legislation. This is the reason why the present work followed the requirements laid down in [5] although this regulation is specific for plastic materials.

The migration testing conditions for materials and articles not yet in contact with food are specified in the Commission Regulation (EU) 2016/1416 [17] which amends the ones established in [5]. The sample shall be placed in contact with the food simulant for a test contact time and at a test contact temperature which should be selected in such a way that they represent the worst foreseeable conditions of use [17].

The migration behaviour of components from paper, cardboard and/or board into Tenax has been compared to the migration into dry foodstuffs such as, for example, fresh fruits [18,19], vegetables [18], cereals, rice [12], salt and sugar [20]. These studies concluded that the food simulant tends to overestimate migration values in comparison with food, so the results obtained with the simulant have a safe margin for consumer protection. In fact, Zurfluh et al. [21] stated that Tenax is a much stronger adsorbent than dry foodstuffs.

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In this work, Tenax was used for the determination of four plasticizers (butylated hydroxytoluene (BHT), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP)) together with benzophenone (BP), which is an ultraviolet (UV) stabilizer, by gas chromatography/mass spectrometry and PARAFAC using DiBP-d_4 as internal standard (IS). Specific migration limits (SMLs) have been set for these analytes in [5].

Plasticizers are used as additives to improve the flexibility of plastic materials, especially in PVC articles. The most commonly used plasticizers are phthalates which are endocrine disruptors since they interfere with the endocrine and hormone system [22]. In addition, phthalates may be involved in autism spectrum disorders, asthma's pathogenesis and cancer in humans [23]. Certain phthalates are ubiquitous in the environment even in the laboratory due to their widespread use. The problem of the ubiquity of DiBP by a non-constant leaching process in the laboratory was detected and overcome in the determination of plasticizers in a previous work [24]. Phthalates can also easily migrate into food [25]. Therefore, considering their toxicity and ubiquitous presence, reliable analytical methods that allow their identification and quantification should be developed.

The use of antioxidants and UV-absorbers are important to protect plastic materials against degradation [22]. BHT is an antioxidant used in food packaging to slow the degradation from exposure to UV light [26], while benzophenone is widely used as a photoinitiator to cure inks and varnishes with UV light for the printing of packaging materials used in food applications [12] such as printed paper and board.

Different EU countries have transmitted to the Rapid Alert System for Food and Feed (RASFF) [27] several notifications in relation to the migration of BP, DiBP, DEHA and DiNP from food contact materials and the presence of BHT in food and feed over the last years. RASFF has reported 5 notifications for BHT, 23 for BP, 2 for DiBP, 13 for DEHA and 42 for DiNP from 24/08/2004 to 29/06/2017. Some notifications for BP have been transmitted through RASFF due to the migration of this compound from carton boxes containing cereal products. An alert about the migration of BP from ink on cartons containing bags with milk powder and cinnamon powder from Turkey was also sent. The amounts of BP found in this case were 428 µg kg^{-1} for the milk powder and 50.2 mg kg^{-1} for the cinnamon powder.

This work deals first with the study of the effect of some parameters that affect the cleaning and the extraction of Tenax on the recovery of the analytes. Then, another study to determine if Tenax could be reused in this multiresidue determination was carried out. Tenax is an expensive simulant (100 g costs around 3500 euros), so reusing Tenax could be important to avoid high costs in the analyses.

Migration tests were also performed on a printed paper sample intended to come into contact with dry foodstuffs using the polymeric powder Tenax as food simulant.

Up to the authors' knowledge, this is the first time that the PARAFAC decomposition has been carried out with data from analyses of Tenax as food simulant.

2. Material and methods

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2.1. Chemicals

Tenax TA (refined), particle size 60-80 mesh, was obtained from Supelco (Bellefonte, USA) and cleaned up prior to use. All the Tenax used in this work came from the same batch.

Diisobutyl phthalate (CAS no. 84-69-5), diisobutyl phthalate-3,4,5,6-d_4 (CAS no. 358730-88-8; analytical standard), diisononyl phthalate (CAS no. 28553-12-0; ester content ≥ 99%, mixture of C_9 isomers), 2,6-di-tert-butyl-4-methyl-phenol (CAS no. 128-37-0), bis(2-ethylhexyl) adipate (CAS no. 103-23-1) and benzophenone (CAS no. 119-61-9; purified by sublimation), all of 99% or higher purity, were purchased from Sigma-Aldrich (Steinheim, Germany). Acetone (CAS no. 67-64-1; for liquid chromatography Lichrosolv®) and n-hexane (CAS no. 110-54-3; for liquid chromatography Lichrosolv®) were obtained from Merck KGaA (Darmstadt, Germany).

2.2. Standard solutions

Stock solutions of DiBP, DEHA and DiNP at 2000 mg L^{-1}, of BHT and BP at 1000 mg L^{-1}, and of DiBP-d_4 at 700 mg L^{-1} were prepared individually in hexane. Intermediate solutions at the concentrations needed in each experimental stage were prepared from the former ones by dilution in the same solvent. All these solutions were stored in crimp vials at low temperature (4ºC) and protected from light. The concentration ranges and number of the standards and/or samples analysed as well as the dimensions of the data tensors evaluated in each experimental stage of this work (Sections 4.1 to 4.4) are collected in Table 1.

It is important to highlight that only laboratory glassware thorough cleaned was used and plastic consumables were avoided as far as possible to try to minimize cross-contamination from plasticizers.

2.3. Experimental procedure

2.3.1. Cleaning of Tenax

Tenax (5 g) was placed into a cellulose thimble and cleaned with 65 mL of acetone in a Soxhlet apparatus for 6h. Next, the Tenax was taken out from the thimble and placed into a Petri dish which was then closed and put under the fume hood to evaporate most of the solvent. The covered Petri dish was finally placed into an oven at 160°C for 6h. After heating, the Tenax was stored in a glass desiccator until its use.

2.3.2. Spiked Tenax samples

In a 40-mL glass vial, 1 g of clean Tenax was placed and the appropriate volume of the solutions of each of the analytes was added to obtain one of the following final concentration levels (depending on the stage of this work): 25 or 50 µg L^{-1} for BHT and BP, 50 or 100 µg L^{-1} for DiBP and DEHA, and 2 or 4 mg L^{-1} for DiNP. After 15 min, the Tenax was extracted following the procedure described in Section 2.3.4.

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2.3.3. Migration test sample preparation

A printed paper sample intended to come into contact with dry foodstuffs was cut into round pieces with a diameter of 48 mm and each piece was placed into a Petri dish. Next, 1 g of clean Tenax was distributed over the circular piece to cover the paper sample completely. The Petri dish was closed, wrapped with aluminium foil carefully to keep the paper sample covered with the Tenax and placed into an oven at 70ºC for 24 h. At the end of the migration period, the Petri dish was removed from the oven, allowed to reach room temperature and the Tenax was transferred carefully into a 40-mL vial.

2.3.4. Extraction of the Tenax

1 g of Tenax (clean, spiked or the one contained in the Petri dish after the migration test) was transferred into a 40-mL vial and 10 mL of hexane was added. The vial was shaken with the agitator needed in each experimental stage of this work for the specified time in each case and then was left to settle for 5 min. A fritted funnel with a glass microfiber filter was inserted into a new 40-mL vial and the hexane was decanted through the filter. 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. A portion of the extract was transferred to a 2-mL amber glass vial and injected into the GC/MS system.

2.4. GC/MS conditions

A volume of 1 µL was injected at a controlled speed of 1 µL s^{-1} with an injection penetration of 40 mm. Before and after each injection, the syringe was washed twice with acetone and twice with hexane. The PTV inlet operated in the cold splitless mode. Helium was used as the carrier gas at a constant flow of 1.3 mL min^{-1}, and the initial pressure was 10.121 psi. During the injection, the inlet temperature was held at 55ºC for 0.1 min. For cold splitless mode, an initial inlet temperature below the boiling point of the solvent is recommended [28,29,30]. The first inlet temperature ramp started at 0.1 min since this provides good transfer and reproducibility [28]. This temperature was ramped then at 12ºC s^{-1} up to 270ºC, which was held for 15 min. The septum purge flow rate was fixed at 3 mL min^{-1} while the purge flow rate through the split vent was 30 mL min^{-1} from 0.6 min to 2 min. After 2 min, the flow rate was set at 20 mL min^{-1}.

Initially, the column was maintained at a low temperature (below the boiling point of the solvent) to re-condense and re-focuse the analytes [30]. The oven temperature was 40ºC for 0.6 min after injection and then increased at 20ºC min^{-1} to 250ºC, which was maintained for 1 min and next ramped again at 10ºC min^{-1} to 290ºC, which was held for 3 min. The run time was 19.1 min. A post-run step was carried out at 300ºC for 4 min.

The mass spectrometer operated in the electron impact (EI) ionization mode at 70 eV. The transfer line temperature was fixed at 300°C, whereas those of the ion source and the quadrupole were, respectively, 230°C and 150°C. After a solvent delay of 8 min, data were acquired in single ion monitoring (SIM) mode using five acquisition windows: i) for BHT (start

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time: 8 min, ion dwell time: 30 ms), the m/z ratios recorded were 91, 145, 177, 205 and 220; ii) for BP (start time: 8.80 min, ion dwell time: 30 ms), the m/z ratios selected were 51, 77, 105, 152 and 182; iii) for DiBP and DiBP-d_4 (start time: 9.80 min, ion dwell time: 10 ms), where the diagnostic ions for DiBP were 104, 149, 167, 205 and 223, and the diagnostic ions for DiBP-d_4 were 80, 153, 171, 209 and 227; iv) for DEHA (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 (start time: 14.60 min, ion dwell time: 25 ms), the diagnostic ions were 57, 127, 149, 167, 275 and 293.

2.5. Instrumental

The cleaning of Tenax was performed in an apparatus for Soxhlet extraction DET. GRAS N with 6 places (JP Selecta S.A., Barcelona, Spain) using the cellulose thimbles PRAT DUMAS (26 mm inner diameter, 30 mm outer diameter, 60 mm height) (Couze-et-Saint-Front, France). The migration cells were Duroplan Petri dishes made of Duran® borosilicate glass (60 mm outer diameter × 20 mm height) which were purchased from Sigma-Aldrich (Steinheim, Germany). An oven Conterm (JP Selecta S.A., Barcelona, Spain) was used to dry the Tenax after its cleaning and to perform the migration testing. The four different modes of agitation evaluated with the two-way analysis of variance (ANOVA) were: an orbital shaker Rotabit which was purchased from JP Selecta S.A. (Barcelona, Spain), a vortex mixer LBX Instruments V05 series with speed control (Barcelona, Spain), a rocking mixer Vibromatic equipped with 8 clamps (JP Selecta S.A., Barcelona, Spain) and a magnetic stirrer GERSTEL 20 Position Twister Stir Plate (Mülheiman der Ruhr, Germany). For the extraction step, fritted funnels made of borosilicate glass with a diameter of 47 mm (Boroglass S.L., Barcelona, Spain) were used together with the Whatman® glass microfiber filters (GF/A grade, 47 mm diameter) which were obtained from GE Healthcare (Little Chalfont, UK).

Analyses were carried out on an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrometer detector (Agilent Technologies, Santa Clara, CA, USA). The gas chromatograph was equipped with an Agilent HP-5MS Ultra Inert (30 m × 0.25 mm i.d., 0.25 µm film thickness) analytical column. The injection system consisted of a 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. Injections were performed using the MultiPurpose Sampler MPS2XL from GERSTEL with a 10 µL syringe.

2.6. Software

MSD ChemStation version E.02.01.1177 (Agilent Technologies, Inc.) with Data Analysis software was used for data acquisition and processing. The NIST mass spectral library [31] was also used. PARAFAC decompositions were performed with the PLS_Toolbox 6.0.1 [32] for use with MATLAB [33] (The MathWorks, Inc.). The regression models were fitted and validated and the two-way ANOVA as well as the paired sample t-test were performed using STATGRAPHICS Centurion XVI [34]. Decision limit (CCα) and capability of detection (CCβ) were determined using the DETARCHI program [35].

3. Theory

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3.1. PARAFAC decomposition

GC/MS data can be arranged for each chromatographic peak in a three-way array **X** and analysed with the PARAFAC decomposition technique. In this case, the dimension of the data tensor **X** is $I \times J \times K$, where for each of the K samples analysed, the abundance measured at J m/z ratios is recorded at I elution times around the retention time of every compound. PARAFAC decomposes a GC/MS data tensor **X** into trilinear factors [36] and each factor consists of three loading vectors $\mathbf{a}_f$, $\mathbf{b}_f$ and $\mathbf{c}_f$. 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.

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

GC/MS data are trilinear if the experimental data tensor is compatible with the structure in Eq. (1). The core consistency diagnostic (CORCONDIA) [37] measures the trilinearity degree of the experimental data tensor. If the data tensor is trilinear, then the maximum CORCONDIA value of 100 is achieved. The PARAFAC least squares solution is unique when the data tensor is trilinear and the appropriate number of factors has been chosen to fit the PARAFAC model. The uniqueness property makes it possible to identify compounds unequivocally by their chromatographic and spectral profiles as laid down in some official regulations and guidelines [38,39,40], even if an coeluent that shares ions with the analyte of interest is present [41,42,43].

4. Results and discussion

4.1. Tolerance intervals for the unequivocal identification of the analytes

The confirmatory criteria for chromatographic methods laid down in EUR 24105 EN [38] were followed in this work to guarantee the unequivocal identification of every analyte. Ten reference standards were first prepared and analysed to establish the permitted tolerance intervals. Five of these samples contained the analytes at five different concentration levels and the IS at a fixed concentration, whereas the rest of the samples contained the analytes at a fixed concentration and the IS at five concentration levels. The concentration ranges of these standards are included in the first row of Table 1 (third column). In addition, three system blanks (without injecting a solvent) at the beginning, middle and end of the analytical sequence and a solvent blank without IS (only hexane) were injected to verify the GC/MS system performance. After baseline correction, the chromatograms obtained from all these 14 samples were fragmented around the retention time of each analyte and the resulting data matrices were arranged together into a three-way tensor for each analyte, except for

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DiBP and DiBP-d_4 peaks, for which only one tensor was considered for both compounds simultaneously. Then, a PARAFAC decomposition of these five data tensors was performed. The dimensions of each tensor are included in Table 1 (first row, columns 4-8), while the features of the PARAFAC model obtained in each case are listed in Table 2 (second column). The PARAFAC decomposition of each tensor provides a unique chromatographic and spectral profile for every compound that is common to all the samples. This allowed the estimation of the tolerance intervals according to [38]. So, 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 calculated using the retention time of each analyte obtained through the chromatographic profile (see Table 2, columns 3-5). It must be noticed that it was not possible to establish a retention time for DiNP since this analyte has a finger-peak chromatographic signal (see Fig. 1 (a)). The tolerance intervals for the relative ion abundances of each m/z ion with regard to the base peak were calculated with the spectral loadings (see Table 2, columns 6-9). Both intervals were used as reference for the unequivocal identification of the analytes in the following stages of this work.

4.2. Study of some parameters affecting the cleaning/extraction of Tenax

4.2.1. Evaluating the effect of the Soxhlet position and the fritted funnel on the recovery of the analytes

In this work, the Soxhlet apparatus used for the cleaning procedure had six places in which one thimble could be put in each of them. Therefore, it is possible with this apparatus to clean Tenax placed into 6 different thimbles with acetone at the same time.

In a first step, a study to evaluate the effect of a parameter of the cleaning procedure (the place of the Soxhet in which the Tenax was cleaned) and a parameter of the extraction procedure (the fritted funnel) on the recovery of each analyte was proposed. So, a total of 30 g of Tenax was cleaned (5 g in each of the 6 places of the Soxhlet) according to the detailed procedure included in Section 2.3.1. Four spiked Tenax samples were prepared with the Tenax cleaned in each position of the Soxhlet to contain finally 25 μg L^{-1} of BHT and BP, 50 μg L^{-1} of DiBP and DEHA, and 2 mg L^{-1} of DiNP (see Section 2.3.2). Then, the 4 samples prepared for each cleaning position were extracted following the procedure described in Section 2.3.4 using 4 fritted funnels. In this part of the study, the vials were shaken manually for 20 seconds and an orbital shaker was also used at 180 oscillations min^{-1} for 5 min in each extraction step. The 24 extracts were injected twice in the GC/MS system. Six extracts of Tenax blanks (one for each of the 6 places) were also prepared to check if the analytes were already present in the Tenax. These blanks were prepared using the same fritted funnel. In addition, 12 solvent standards at 12 concentration levels were prepared within the concentration ranges detailed in Table 1 (second row, third column). Three of these solvent standards were replicated. The ubiquity of DiBP in the laboratory was confirmed in a previous work [24] since this analyte appeared in a different quantity in each solvent blank injected. In this work, the concentration of DiBP in the lowest standard was at 25 μg L^{-1} since this concentration was proved to be statistically different from the blank concentration ($\alpha = \beta = 0.012$) in our laboratory [24]. Five three-way tensors containing the data from the analyses of all these samples together with 10 solvent blanks and 20 system blanks without containing

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IS, measured throughout the analytical sequence, were thus built. The dimensions of these data tensors appear in Table 1 (second row, columns 4-8) for each analyte. The abundance of DiBP is much greater than the abundance of the IS at the studied concentrations. In this case, PARAFAC needs a greater variation of DiBP-d_4 to obtain an adequate model so 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 the internal standard (75 μg L^{-1} of DiBP-d_4) was added to the tensor of DiBP and DiBP-d_4, as can be seen in the table note (a) of Table 1.

The PARAFAC decomposition of the tensor built for BHT, BP and DEHA resulted in an unconstrained one-factor model in each case. A two-factor model, where the chromatographic and spectral profiles had been non-negativity-constrained, was needed for DiBP and the IS. In the case of DiNP, the PARAFAC decomposition of its tensor yielded a two-factor model (CORCONDIA index of 100%), where the non-negativity constraint was imposed for the three modes. The first factor in this model (in dark blue in Fig. 2) was associated to DiNP, whereas the second one (in light green in Fig. 2) was the baseline which appeared although a previous correction had been made for the chromatograms. The signal of DiNP appeared in the chromatogram (Fig. 2 (a)) as finger peaks because of an array of possible C_9 isomers. A high number of scans (823) was considered for this analyte since it took about 2 min to elute as can be seen in this last figure. The characteristic m/z ratio of the baseline was 57, which was also shared with DiNP (see Fig. 2 (b)). For DiNP, the sample loadings (Fig. 2 (c)) for the solvent standards were coherent considering the concentration of these calibration samples. DiNP was not contained in the Tenax since its sample loadings were zero for the blanks. In addition, DiNP did not appear in the system and solvent blanks measured between the different types of samples analysed. As can be seen in this figure, the sample loadings of DiNP in the spiked Tenax samples varied depending on the place in which the Tenax was cleaned. However, these loadings remained constant for the first place of the Soxhlet. The sample loadings of the baseline were nearly zero in the system blanks and they were higher and remained constant for the rest of the samples.

The results of the chromatographic and spectral identification of every analyte appear in Table 3 (third column). The values of the relative retention times and the relative ion abundances were within the corresponding tolerance intervals used as reference (see Table 2) in all cases except for the m/z ratio 209 for DiBP-d_4. However, all the analytes were unequivocally identified since at least 3 m/z ratios met the identification conditions.

Next, the sample loadings of each analyte were standardized by dividing each of them by the corresponding of its internal standard and calibration models “standardized sample loading versus true concentration” were fitted and validated for each analyte. Table 3 (fourth column) shows the parameters of the linear least squares (LS) regression models. A quadratic regression model was considered for BP and DiNP. One outlier was detected in the calibration models for BHT and BP since they had a studentized residual greater than 3 in absolute value, so they were removed and a new LS fitting was performed and validated with the remaining data in both cases. In all cases, the regression models were significant and there was not lack of fit at a 95% confidence level. As can be seen in the fifth column of Table 3, the lowest mean of the absolute value of the relative errors in calibration was 2.43% (n = 10) for BHT, while the highest value was obtained for BP (4.52%, n = 10). These values were calculated excluding the samples with predicted concentrations lower than CCβ. Then, the accuracy lines were performed, that is, the regressions “predicted concentration versus

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true concentration" (see Table 3, column 6). The property of trueness was fulfilled for all the analytes at a 95% confidence level since the intercept and the slope were significantly equal to 0 and 1, respectively. The values of CCα and CCβ are also listed in Table 3 (two last columns), being the probabilities of false positive (α) and false negative (β) fixed at 0.05. The CCβ values ranged from 5.86 to 262.2 μg L^{-1}. The procedure to estimate CCβ from three-way data can be found in [44].

The regression models "standardized sample loading versus true concentration" enabled to determine the quantity of every analyte in the blanks and spiked samples. The confidence intervals for the predicted concentration of DiBP, DEHA and DiNP in the Tenax blanks included zero, while the amount of BP found was lower than CCβ. Therefore, none of these four analytes was detected in the blanks. However, BHT was contained in these blanks, being 7.60 μg L^{-1} the value of the average concentration for this analyte. The recovery rates for every analyte in each of the spiked samples were estimated taking into account that the blank average value for BHT must be subtracted to determine the amount of this analyte in each sample.

A two-way ANOVA [45] was performed considering two factors (Soxhlet position at 6 levels and the fritted funnel at 4 levels, with two replicates) and the interaction between both factors, where the response variable was the recovery. In this study, it could be concluded that both factors and the interaction had a statistically significant effect on the recovery of each analyte at a 95% confidence level, since the null hypothesis (H_0) of the ANOVA F-test states that there is no effect and the corresponding p-values were lower than 0.05. It must be taken into account that the factor related to the fritted funnel in this study was actually the whole extraction procedure. As can be seen in Table 4, which contains some results of this ANOVA, the percentages of the total variance of the response due to the effect of the Soxhlet position were high for all the analytes, particularly for BHT and BP. The first place of the Soxhlet was chosen for cleaning Tenax in future analyses since the values of the coefficient of variation of the recovery obtained in this position were lower than for the rest. This agreed with the sample loadings of Fig. 2 (c).

4.2.2. Selection of the optimum mode of agitation through a two-way ANOVA

According to one of the conclusions of Section 4.2.1, the whole extraction procedure had a significant effect on the recovery of the analytes. Therefore, another ANOVA was used to evaluate two factors related to the extraction step. The possible interaction between both factors was also considered. The mode of agitation (factor 1) was studied at 4 levels: an orbital shaker together with manual stirring as in Section 4.2.1 (mode of agitation 1), a vortex mixer working for 2 min (mode of agitation 2), a rocking mixer for 15 min (mode of agitation 3) and a magnetic stirrer at 1500 rpm for 15 min (mode of agitation 4) in each extraction step. All of them enabled the preparation of the samples simultaneously, except for the vortex mixer since in this case only one sample could be prepared at a time. The second factor was the 4 fritted funnels used in Section 4.2.1, two replicates were considered and the response variable was the recovery of each analyte.

For each mode of agitation, four spiked Tenax samples (at the same concentration of the analytes as in Section 4.2.1) were prepared with Tenax cleaned in the place number 1 of the

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Soxhlet and extracted using the four fritted funnels. These samples were analysed in duplicate. A Tenax blank was also prepared with each mode of agitation using a single fritted funnel. Two solvent calibrations were performed since a change in the conditions of the GC/MS system occurred during the analysis of all these samples. So, 15 solvent standards at 12 concentration levels (three of them replicated) were prepared within the concentration ranges detailed in Table 1 (third row, third column) for each calibration set. The first calibration set was used for the samples prepared with the orbital shaker together with manual stirring, while the second one was used for the rest of the samples. In addition, some system and solvent blanks were injected to control the performance and cleanliness of the GC/MS equipment throughout the analytical sequence. Two standards 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 the internal standard (75 μg L^{-1} of DiBP-d_4) were also added to the tensor of DiBP and DiBP-d_4 to obtain an adequate PARAFAC model. Table 1 (third row, columns 4 to 8) shows the dimensions of the data tensors built with all these samples, whereas some features of the model estimated from the PARAFAC decomposition of every tensor are listed in Table 5 (second column). The PARAFAC model of DiBP and DiBP-d_4 is explained in detail in the supplementary material (Fig. S1).

Unequivocal identification of every analyte was carried out by verifying that the relative abundances obtained from the loadings of the spectral profiles and the relative retention times (see Table 5, third column) were within the tolerance intervals established previously in Section 4.1 (see Table 2).

Table 5 contains the parameters of the regression models “standardized sample loading versus true concentration” fitted and validated for every analyte with the first calibration set (columns 4-5 of this table) and with the second one (columns 6-7 of Table 5). The analyses of the confidence ellipses for the slope and the intercept of the accuracy line are included in the supplementary material (see Fig. S2).The trueness of the analytical method was ensured in all cases at a 95% confidence level (a 97% confidence level for BP in the second calibration set) since all the confidence ellipses contained the point (0,1).

The concentration of each analyte in the blanks and spiked samples prepared using the mode of agitation 1 was determined from the corresponding regression model “standardized sample loading versus true concentration” related to the first calibration set, while the concentration of the rest of the samples was determined with the corresponding regression model related to the second calibration set. As in Section 4.2.1, BHT was the only analyte contained in the Tenax at a concentration of 11.54 μg L^{-1}, 11.27 μg L^{-1}, 9.40 μg L^{-1} and 23.59 μg L^{-1} in the blanks prepared using the mode of agitation 1, 2, 3 and 4, respectively. For this analyte, the recovery rates were calculated taking the concentration of the blank away from the concentration of each spiked sample prepared with the same mode of agitation.

In this two-way ANOVA, the mode of agitation, the fritted funnel and the interaction between them had a statistically significant effect on the recovery of the analytes at a 95% confidence level.

The values of the average recovery rate and the coefficient of variation obtained with each mode of agitation are given in Table 6 for every analyte. The recovery rates of BHT obtained with mode of agitation 4 in two cases were extremely high, that is the reason why the coefficient of variation was so high in this case. As can be seen in Table 6, the coefficient of

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variation of DEHA with mode 3 was not acceptable and the average recovery of BHT with mode 2 was the lowest for this analyte. On the other hand, the lowest values of the coefficient of variation were obtained with mode of agitation 1 for every analyte, except for DiBP. The best values of the average recovery of BHT, BP and DiNP were achieved with mode of agitation 4 although their values of the coefficient for variation were higher than with mode 1. Therefore, mode 1 and 4 would be the most suitable ones. However, mode 1 may not be enough to extract all the amount of the analytes from the Tenax since the simulant moved gently with this mode. On the other hand, although mode 4 seemed to move the solid more violently than in mode 1, after a few seconds using mode 4, the Tenax began to stick to the walls of the vial due to its static electricity.

So, in order to try to improve the results, especially the recovery value of DEHA, some changes were considered for the mode of agitation 1 and 4. The time of the orbital shaker in mode 1 was increased (15 min instead of 5 min), whereas the time was decreased in mode 4 (7 min 30 s instead of 15 min) and during this time this stirring mode was stopped each 30 s in order to enable the solid particles to settle down under the action of gravity to prevent adhesion to glass and it was turned on again after 5 s. The change considered in mode 1 was named as the new mode of agitation 5, while the change in mode 4 was named as mode of agitation 6. For these new modes of agitation, a Tenax blank and four spiked Tenax samples were prepared in each case as explained previously in this same Section. As always, the spiked samples were analysed in duplicate. Then, the samples related to modes 2 and 3 were removed from the data tensors built before (see Table 1, third row) and the new samples of mode 5 and 6 were included, so the dimension of the new data tensors remained the same except for the tensor of DiBP and DiBP-d_4 where only one of the two added samples in the previous case was needed (see Table 1, third row, column 6).

An unconstrained one-factor model was needed for BHT (explained variance of 99.05%), BP (explained variance of 86.19%) and DEHA (explained variance of 98.19%). The presence of these analytes was guaranteed in terms of retention time and mass spectrum in each case. The PARAFAC model for DiBP and the IS required two factors, being the first and second factors unequivocally linked to DiBP and DiBP-d_4, respectively (explained variance of 98.90%, CORCONDIA index equal to 91%), where the chromatographic and spectral modes had been non-negativity-constrained. Regarding DiNP, a two-factor PARAFAC model was estimated (explained variance of 99.72%, CORCONDIA of 100%) after a non-negativity constraint had been imposed on the chromatographic, spectral and sample ways. In this model, the first factor was related to the baseline, while the second one was unequivocally associated to DiNP.

The parameters of the two regressions estimated for each analyte between the standardized sample loadings of every analyte (obtained through these last PARAFAC decompositions) and the concentration of the solvent standards were quite similar to those presented in Table 5 for the previous case. The concentration of the samples prepared with mode of agitation 1 was calculated using the first regression model, while the second regression was used for the samples prepared with modes 4, 5 and 6. Trueness was verified in all cases at a 95% confidence level, except for the second regression for BP in which the property of trueness was fulfilled at a 97% confidence level.

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The concentration of BHT found in the Tenax blanks was 10.00 μg L^{-1} and 11.23 μg L^{-1} for the ones prepared with modes 5 and 6, respectively.

The optimum mode of agitation was selected through another two-way ANOVA. In this case, the mode of agitation (at 4 levels: modes 1, 4, 5 and 6) and the fritted funnel (at 4 levels) together with the interaction between both of them also had a significant effect on the recovery of BHT, DiBP, DEHA and DiNP. However, only the mode of agitation had effect on the recovery of BP. Table 7 collects some results of this ANOVA. As can be seen in this table, the highest percentages of the total variance of the response corresponded to the mode of agitation in all cases except for BHT. The values of the recovery and the coefficient of variation for modes 1 and 4 in Tables 6 and 7 were calculated with two different PARAFAC decompositions. This is the reason why there were slight differences in these values between Table 6 and 7 despite the samples were the same in both cases. Taking the values of the recovery and the coefficient of variation into account (see Table 7), the best option for DEHA and not so bad for the others was mode of agitation 6. Therefore, a magnetic stirrer operating in discontinuous mode was chosen for future analyses.

4.3. Study of the reuse of Tenax

The Tenax used in the previous stages of this work had been cleaned only once since its cleaning is a requirement before its use. However, this simulant is expensive, so its reuse would save costs. But the consecutive cleanings might lead to some changes in the conditions Tenax should fulfil. So, a study to evaluate if Tenax could be reused was proposed. The aim was to determine: i) if some analytes remain in Tenax when it is reused and ii) the effect that the cleaning procedure may have in the adsorption capability of this simulant.

Fig. 3 depicts the experimental stages followed to carry out this study. For each column of this figure, 4 samples were prepared with Tenax cleaned (a specific number of times) in the first place of the Soxhlet, extracted using four fritted funnels and a magnetic stirrer operating in discontinuous mode (as explained in Section 4.2.2) and injected in duplicate in the GC/MS system.

For this study, 8 Tenax blanks (column A of Fig. 3) and 8 spiked Tenax samples (column B of Fig. 3) were first prepared using the simulant cleaned only once. After the analysis of these 16 samples, the Tenax used to prepare the blanks was cleaned again and new spiked samples were prepared with it (column C of Fig. 3). On the other hand, the Tenax used for the spiked samples of column B was cleaned again and blank samples were prepared with it this time (column D of Fig. 3). After the analysis of these blanks, the corresponding amount of Tenax was cleaned again and spiked samples were prepared (column E of Fig. 3). Therefore, the columns C and D corresponded to Tenax cleaned twice, whereas the column E was related to Tenax cleaned three times. The amount of the analytes added to prepare the spiked samples was the same as in Section 4.2.1 and 4.2.2 which will be named as concentration level 1. The whole study was repeated again at a higher concentration of the analytes indicated in Section 2.3.2 (concentration level 2) in order to check if the cleaning procedure was suitable.

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Table 1 (fourth row, third column) shows the concentration ranges for each compound in the 15 calibration standards prepared. On the other hand, several system and solvent blanks together with 8 solvent standards were injected to test the performance of the GC/MS system throughout the analytical sequence. All these samples were arranged in data tensors whose dimensions are specified in Table 1 (fourth row, columns 4-8). Three additional standards were needed to obtain an adequate PARAFAC decomposition of the tensor of DiBP and DiBP-d_4: two of them contained 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 75 μg L^{-1} of DiBP-d_4, while the other sample only contained the IS at a higher concentration (100 μg L^{-1}).

Next, the PARAFAC decomposition of each data tensor was performed. The most remarkable characteristics of every PARAFAC model are collected in the second column of Table 8.

The need to cut the GC column due to maintenance tasks prior to starting the analysis of the samples of this section led to a variation in the absolute retention times regarding the ones obtained with the reference standards. However, the tolerance intervals used as reference for the identification of the analytes were calculated for the relative retention time. This guaranteed the unequivocal identification of each analyte since the relative retention times obtained in this section for each analyte (see Table 8, third column) lay within the tolerance intervals established previously (see Table 2).

The parameters of the calibration model and accuracy line obtained for each analyte are collected in Table 8. As can be seen in this table, the p-values of the hypothesis test for the intercept and the slope of the accuracy line were higher than 0.05 so the intercept and the slope were significantly equal to 0 and 1, respectively, and the property of trueness was fulfilled.

Next, a paired sample t-test was performed to compare the predicted concentration of each analyte in the blanks prepared with Tenax cleaned once and twice (columns A and D of Fig. 3, respectively). The results of this test will determine if the cleaning procedure of Tenax was adequate or not. On the other hand, the predicted concentration of each analyte in the spiked samples prepared with Tenax cleaned once, twice and three times (columns B, C and E of Fig. 3, respectively) were also compared in pairs through a paired sample t-test for each concentration level. In this case, this last comparison evaluates if the consecutive cleanings of Tenax affect its adsorption capability. In this way, the effect of the fritted funnel was obviated since the paired sample t-test was carried out. The null hypothesis (H_0) of this test is that the mean difference between the paired samples is equal to zero, whereas the alternative hypothesis (H_a) poses that the mean is not equal to zero. Fig. 4 and Fig. 5 represent the values of the predicted concentration of each analyte in each of the blanks and the spiked samples, respectively, while the results of this test are collected in Table 9.

The mean of the differences between the blanks for BHT was significantly different from zero at a 95% confidence level since the p-values were lower than 0.05 as can be seen in Table 9. In addition, the initial amount of this analyte found in the blanks related to the first cleaning of Tenax nearly disappeared after the second cleaning, so the simulant was better cleaned in this last case, as can be seen in Fig. 4. The amount of BHT found in the blanks prepared together with the spiked samples at the concentration level 2 was higher than in the concentration level 1 (see Fig. 4). This could be due to the use of Tenax from a different

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container although all the Tenax used in this work came from the same batch. In the case of the spiked samples, there were significant differences between the second and the first cleaning and the average values were negative so the extraction of BHT decreased with the consecutive cleanings as can be seen in Fig. 5. Therefore, the reuse of Tenax is not possible if BHT is going to be determined.

The amount of BP found in all the blanks was below CCβ. In addition, this amount decreased with the second cleaning for the first concentration level (see Fig. 4) and remained the same for the concentration level 2 as can be seen in Table 9. The cleaning affected the adsorption capability since the differences between all the pair of spiked samples were significant and this capability decreased with the consecutive cleanings of the Tenax as can be seen in Fig. 5. So, clearly, Tenax cannot be reused in the analysis of BP.

In the case of DiBP, Tenax was better cleaned when it was cleaned twice for the concentration level 1, whereas the amount of this analyte in the blanks of the concentration level 2 was below CCβ (see Fig. 4). As can be seen in Table 9, there were only no significant differences between the spiked samples for the first concentration level. So, Tenax could be reused if the concentration of DiBP is similar to the ones of the concentration level 1.

The amount of DEHA contained in the blanks was below CCβ. On the other hand, taking into account the p-values for the comparison of the spiked samples in Table 9, it could be concluded that Tenax could only be reused in the analysis of DEHA when the concentration of this analyte is not higher than the ones considered in the concentration level 1 and only two cleanings could be performed.

Lastly, in the case of DiNP, the amount in the blanks was also below CCβ and Tenax cannot be reused with this analyte since its extraction decreased with the second cleaning of Tenax in both concentration levels (see Table 9).

Therefore, this study led to the conclusion that Tenax cannot be reused in this multirresidue analysis. In addition, the cleaning procedure was adequate since none of the analytes appeared at a concentration higher than in the blank related to the first cleaning, even when the simulant had been previously used to prepare spiked samples.

4.4. Migration from a printed paper sample

The migration of the analytes considered in this work from 5 printed paper replicates into Tenax was studied. The migration tests were conducted at 70ºC for 24 h as explained in Section 2.3.3. These migration conditions were selected according to [17] since they represent the worst foreseeable conditions of intended use of the paper sample under examination. Then, the corresponding extracts were obtained following the extraction procedure as detailed in Section 2.3.4. A magnetic stirrer operating in discontinuous mode was used in the extraction procedure (see Section 4.2.2). In addition, two Tenax blanks were also prepared following the same migration test and extraction procedure as the paper replicates but in this case Tenax was not into contact with the paper. To carry out these analyses, 10 g of Tenax were needed so Tenax that had not been used before were cleaned (as explained in Section 2.3.1) in the first place of the Soxhlet and then combined to eliminate the variability. Seven solvent standards, at the concentration ranges listed in Table

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1 (fifth row, third column) for every analyte, were also analysed to quantify the amount migrated from the paper in each case. Fig. 1 (a) shows the total ion chromatogram (TIC) of the calibration standard injected at the highest concentration.

As always, both system and solvent blanks were included in the analytical sequence. From the comparison between the TIC of the calibration standard shown in Fig. 1 (a), the TIC of the extract obtained after the migration test of one of the paper replicates and the TICs of the system blanks injected before (in black in Fig. 1 (b)) and after this extract (in red in Fig. 1 (b)), it is clear that the analytes did not appear in the system blanks.

After data processing, five tensors whose dimensions are collected in Table 1 (fifth row, columns 4-8) were built. In order to obtain an adequate PARAFAC model, a standard containing only the IS at a higher concentration than the rest of the samples (100 μg L^{-1}) was added to the tensor of DiBP and DiBP-d_4. The characteristics of the PARAFAC decompositions performed for each tensor are listed in Table 10 (second column). By comparing the chromatographic and spectral profiles of the factor associated to each analyte with those used as reference (see Table 2), the presence of every compound was unequivocally confirmed (see Table 10, third column) despite the cut of the GC column performed in Section 4.3.

The equations of the calibration models and the accuracy lines are collected in Table 10 (columns 4 and 5, respectively). Trueness was verified for all the analytes at a 95% confidence level. The values of CCα and CCβ obtained in this stage of the work (see Table 10, columns 6 and 7) were lower than the ones obtained in Section 4.2.1 (see Table 3, columns 7 and 8) with just the exception of BP whose values were similar in both cases. This improvement could be mainly due to the performance of some maintenance tasks in the GC/MS system and the reduction in the concentration range of this calibration. In addition, as can be seen in Table 10, the residual standard deviation of the accuracy lines was lower than in Section 4.2.1 (see Table 3).

The values of the average concentration found of each analyte in the Tenax blanks and in the paper together with the corresponding standard deviation are collected in Table 10 (columns 8 and 9). The sample loadings of DiNP for those samples were zero so DiNP was not detected. As can be seen in Table 10, the average concentration of BP and DEHA was below their corresponding CCβ values. On the other hand, the amount of DiBP was below the first standard fixed at 25 μg L^{-1} so it could not be exactly estimated. However, there was an amount of BHT contained in the Tenax blank. A t-test was used to determine if the average concentration of BHT found in the paper was greater than the average amount found in the Tenax blank. In this case, the null hypothesis of the t-test was that the average concentration in the paper equalled 10.35 (n = 2), whereas the alternative hypothesis posed that the average concentration in the paper was greater than 10.35. Since the p-value for this test was 0.02, it could be concluded that BHT was contained in the paper in an amount significantly greater than that contained in the Tenax blank at a 95% confidence level. Therefore, it was confirmed that the migration of BHT from the printed paper into Tenax had occurred; being 2.56 μg L^{-1} the amount migrated from the paper.

5. Conclusions

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After a preliminary study of some parameters that could affect the cleaning and the extraction of Tenax, it has been stated that the place of the Soxhlet in which Tenax is cleaned together with the mode of agitation and the fritted funnel used in the extraction procedure have a significant effect on the recovery of BHT, BP, DiBP, DEHA and DiNP. The first Soxhlet position and a magnetic stirrer operating in discontinuous mode have been chosen through the results of a two-way ANOVA.

Tenax cannot be reused in the multiresidue analysis performed in this work since the consecutive cleanings of this simulant affect its adsorption capability. However, Tenax can be reused in the determination of DiBP and/or DEHA in certain circumstances.

The presence of BHT has been confirmed in the Tenax blanks and this analyte has also migrated from a printed paper sample into Tenax, being its concentration equal to 2.56 μg L^{-1}.

The unequivocal identification and quantification of each analyte according to the requirements laid down in the EU legislation in force have been possible using the PARAFAC decomposition even in the presence of complex finger-peak signals such as that of DiNP.

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Acknowledgments

The authors thank the financial support provided by Ministerio de Economía y Competitividad (CTQ2014-53157-R) and Junta de Castilla y León (BU012P17). Both of them co-financed with European FEDER funds.

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FIGURE CAPTIONS

Fig. 1 Total ion chromatograms (TICs) obtained from the injection of: (a) a calibration standard containing 45 μg L^{-1} of BHT, BP and DEHA, 75 μg L^{-1} of DiBP, 25 μg L^{-1} of DiBP-d_4 and 2500 μg L^{-1} of DiNP, and (b) the extract obtained after the migration test of the first printed paper replicate (in blue) together with two system blanks: the one injected before this sample is in black, whereas the one injected at the end of the analytical sequence is in red. Peak labels: 1, BHT; 2, BP; 3, DiBP and DiBP-d_4; 4, DEHA; 5, DiNP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

Fig. 2 PARAFAC model with two factors obtained with the data tensor of DiNP built for the study of the effect of the Soxhlet position and the fritted funnel. Loadings of the: (a) chromatographic profile, (b) spectral profile, (c) sample profile (blue: DiNP, light green: baseline). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

Fig. 3 Diagram of the experimental steps followed to perform the study of the reuse of Tenax for a fixed concentration level.

Fig. 4 Values of the predicted concentration of: BHT (first row), BP (second row), DiBP (third row), DEHA (fourth row) and DiNP (fifth row) in each of the Tenax blanks measured in the study of the reuse of Tenax. The left-hand side figures correspond to the ones prepared together with the spiked samples for the concentration level 1, whereas the right-hand side figures correspond to the concentration level 2. The blanks prepared with Tenax cleaned once (column A of Fig. 3) are marked in light blue diamonds, while the blanks prepared with Tenax cleaned twice (column D of Fig. 3) are in red squares. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

Fig. 5 Values of the predicted concentration of: BHT (first row), BP (second row), DiBP (third row), DEHA (fourth row) and DiNP (fifth row) in each of the spiked Tenax samples measured in the study of the reuse of Tenax. The left-hand side figures

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correspond to the concentration level 1, whereas the right-hand side figures correspond to the concentration level 2. The spiked samples prepared with Tenax cleaned once (column B of Fig. 3) are marked in light blue diamonds, the samples prepared with Tenax cleaned twice (column C of Fig. 3) are in red squares and the ones prepared with Tenax cleaned three times (column E of Fig. 3) are represented with light green triangles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

Table 1 Summary of the samples analysed and of the dimensions of the tensors built for each analyte in each stage.

Analytical stage	Samples analysed	Concentration range	Dimension of the data tensor (scans × ions × samples)				
			BHT	BP	DiBP and DiBP-d_4	DEHA	DiNP
Tolerance intervals	3 system blanks, 1 solvent blank without IS, 10 reference standards	10-100 µg L^{-1} for BHT, BP and DiBP-d_4, 25-125 µg L^{-1} for DiBP, 25-120 µg L^{-1} for DEHA, 1-5 mg L^{-1} for DiNP	21 × 5 × 14	42 × 5 × 14	41 × 10 × 14	19 × 5 × 14	823 × 6 × 14
Study of the effect of the Soxhlet position and the fritted funnel	20 system blanks, 10 solvent blanks without IS, 15 solvent standards at 12 concentration levels (3 of them replicated), 6 Tenax blanks, 48 spiked Tenax samples	0-100 µg L^{-1} for BHT and BP 0-125 µg L^{-1} for DiBP, 25 µg L^{-1} for DiBP-d_4, 0-120 µg L^{-1} for DEHA, 0-5 mg L^{-1} for DiNP	21 × 5 × 99	42 × 5 × 99	41 × 10 × 100[a]	19 × 5 × 99	823 × 6 × 99

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Selection of the optimum mode of agitation	16 system blanks, 10 solvent blanks without IS, 30 solvent standards at 12 concentration levels (18 of them replicated), 4 Tenax blanks, 32 spiked Tenax samples	0-100 µg L^{-1} for BHT and BP 0-125 µg L^{-1} for DiBP, 25 µg L^{-1} for DiBP-d_4, 0-120 µg L^{-1} for DEHA, 0-5 mg L^{-1} for DiNP	21 × 5 × 92	42 × 5 × 92	41 × 10 × 94[b] (for the 1st analysis) 41 × 10 × 93[a] (for the 2nd analysis)	19 × 5 × 92	823 × 6 × 92
Study of the reuse of Tenax	22 system blanks, 11 solvent blanks without IS, 23 solvent standards at 12 concentration levels (11 of them replicated), 32 Tenax blanks, 48 spiked Tenax samples at two concentration levels	0-100 µg L^{-1} for BHT and BP 0-125 µg L^{-1} for DiBP, 25 µg L^{-1} for DiBP-d_4, 0-120 µg L^{-1} for DEHA, 0-5 mg L^{-1} for DiNP	21 × 5 × 136	42 × 5 × 136	41 × 10 × 139[c]	19 × 5 × 136	823 × 6 × 136
Migration from a printed paper sample	5 system blanks, 2 solvent blanks without IS, 7 solvent standards at 7 concentration levels, 2 Tenax blanks, 5 printed paper replicates	0-45 µg L^{-1} for BHT, BP and DEHA 0-75 µg L^{-1} for DiBP, 25 µg L^{-1} for DiBP-d_4, 0-2.5 mg L^{-1} for DiNP	21 × 5 × 21	42 × 5 × 21	41 × 10 × 22[d]	19 × 5 × 21	823 × 6 × 21

[a] In this case, a standard containing 25 µg L^{-1} of BHT and BP, 50 µg L^{-1} of DiBP and DEHA, 2 mg L^{-1} of DiNP and 75 µg L^{-1} of DiBP-d_4 was also added to this tensor.

[b] In this case, two standards at the same concentration as the one in table note [a] were also added to this tensor.

[c] In this case, two standards at the same concentration as the one in table note [a] and another one only containing 100 µg L^{-1} of DiBP-d_4 were also added to this tensor.

[d] In this case, a standard containing 100 µg L^{-1} of DiBP-d_4 was also added to this tensor.

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Table 2 Characteristics of the PARAFAC models (number of factors, constraints imposed, explained variance and CORCONDIA index) obtained from the decomposition of the tensors built with the reference samples for each analyte (see Table 1, first row) and tolerance intervals for the relative retention time and for the relative ion abundances estimated from the loadings of the chromatographic and spectral profiles, respectively. The base peak in each case is in bold.

Analyte	PARAFAC model	Retention time			Diagnostic ions			
		t_R (min)	Relative t_R	Tolerance interval	m/z ratio	Spectral loading	Relative abundance (%)	Tolerance interval (%)
BHT	1 factor Unconstrained model Explained variance: 99.75%	8.363	0.808	(0.804-0.812)	91	6.64×10^{-2}	6.91	(3.46-10.37)
					145	1.13×10^{-1}	11.71	(9.37-14.05)
					177	7.52×10^{-2}	7.82	(3.91-11.73)
					205	9.61×10^{-1}	100.00	-
					220	2.30×10^{-1}	23.91	(20.32-27.50)
BP	1 factor Unconstrained model Explained variance: 94.94%	9.163	0.885	(0.881-0.890)	51	1.48×10^{-1}	19.28	(15.42-23.14)
					77	4.46×10^{-1}	58.05	(52.25-63.86)
					105	7.68×10^{-1}	100.00	-
					152	3.05×10^{-2}	3.97	(1.99-5.96)
					182	4.34×10^{-1}	56.44	(50.80-62.08)
DiBP-d_4	2 factors (Factor 2: DiBP-d_4) Non-negativity constraint in modes 1 and 2 Explained variance: 99.19% CORCONDIA: 97%	10.350	1.000	-	80	5.83×10^{-2}	5.85	(2.93-8.78)
					153	9.97×10^{-1}	100.00	-
					171	2.63×10^{-2}	2.64	(1.32-3.96)
					209	1.59×10^{-2}	1.60	(0.80-2.40)
					227	5.14×10^{-2}	5.16	(2.58-7.74)
DiBP	2 factors (Factor 1: DiBP) Non-negativity constraint in modes 1 and 2 Explained variance: 99.19% CORCONDIA: 97%	10.356	1.001	(0.996-1.006)	104	7.76×10^{-2}	7.80	(3.90-11.70)
					149	9.95×10^{-1}	100.00	-
					167	2.79×10^{-2}	2.80	(1.40-4.20)
					205	1.43×10^{-2}	1.44	(0.72-2.16)
					223	5.56×10^{-2}	5.59	(2.80-8.39)

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DEHA	1 factor Unconstrained model Explained variance: 98.56%	13.255	1.281	(1.274-1.287)	112	2.97×10^{-1}	31.50	(26.78-36.23)
					129	9.42×10^{-1}	100.00	-
					147	1.54×10^{-1}	16.30	(13.04-19.56)
					241	4.13×10^{-2}	4.39	(2.20-6.59)
					259	1.68×10^{-2}	1.78	(0.89-2.67)
DiNP	2 factors (Factor 1: DiNP) Non-negativity constraint in the three modes Explained variance: 99.77% CORCONDIA: 100%	---[a]	---[a]	---[a]	57	2.79×10^{-1}	29.56	(25.13-33.99)
					127	9.14×10^{-2}	9.67	(4.84-14.51)
					149	9.45×10^{-1}	100.00	-
					167	8.48×10^{-2}	8.97	(4.49-13.46)
					275	5.50×10^{-3}	0.58	(0.29-0.87)
					293	1.17×10^{-1}	12.33	(9.86-14.80)

[a] It is not possible to establish a retention time for DiNP.

Table 3 Characteristics of the PARAFAC models estimated with the data from the study of the effect of the Soxhlet position and the fritted funnel. Identification of every analyte (relative retention time and the relative abundances for each diagnostic ion in brackets). The m/z ratio which is not within its corresponding tolerance interval is in bold. Parameters of the calibration model and of the accuracy line together with the decision limit (CCα) and capability of detection (CCβ) at $x_0 = 0$ ($\alpha = \beta = 0.05$).

Analyte	PARAFAC model	Identification	Calibration model		Accuracy line	CCα ($x = 0$) ($\mu g\ L^{-1}$)	CCβ ($x = 0$) ($\mu g\ L^{-1}$)
			Model (R^2, s_{yx}) (Outliers/standards)	Error (%)[b]	Model (R^2, s_{yx})		
BHT	1 factor Unconstrained model Explained variance: 99.84%	$t_{R,rel}$ = 0.80891 (6.94%) 145 (11.79%) 177 (7.99%) 205 (100%) 220 (23.91%)	$y = -3.93 \times 10^{-2} + 2.95 \times 10^{-2}\, x$ (99.82%, 4.54×10^{-2}) (1/15)	2.43% (n=10)	$y = -1.29 \times 10^{-3} + 1.00\, x$ (99.82%, 1.54)	2.99	5.86
BP	1 factor Unconstrained model Explained variance: 90.36%	$t_{R,rel}$ = 0.88651 (18.96%) 77 (58.06%) 105 (100%) 152 (4.10%) 182 (56.82%)	$y = -1.72 \times 10^{-2} + 2.61 \times 10^{-3}\, x + 4.28 \times 10^{-4}\, x^2$ (99.69%, 7.37×10^{-2}) (1/15)	4.52% (n=10)	$y = 1.32 + 0.98\, x$ (99.39%, 2.47)	4.92	9.65

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DiBP-d_4	2 factors (Factor 2: DiBP-d_4) Non-negativity constraint in modes 1 and 2 Explained variance: 98.53% CORCONDIA: 52%	$t_{R,rel}$ = 1.000 80 (6.19%) 153 (100%) 171 (2.75%) **209** (2.65%) 227 (5.22%)	Internal standard		Internal standard		
DiBP	2 factors (Factor 1: DiBP) Non-negativity constraint in modes 1 and 2 Explained variance: 98.53% CORCONDIA: 52%	$t_{R,rel}$ = 1.001 104 (7.67%) 149 (100%) 167 (2.82%) 205 (1.44%) 223 (5.71%)	$y = 2.62 \times 10^{-1} + 1.77 \times 10^{-2} x$ (99.25%, 5.96×10^{-2}) (0/15)	4.20% (n=14)	$y = 2.40 \times 10^{-3} + 0.99 x$ (99.25%, 3.36)	6.84	13.44
DEHA	1 factor Unconstrained model Explained variance: 98.03%	$t_{R,rel}$ = 1.281 112 (32.93%) 129 (100%) 147 (16.47%) 241 (4.35%) 259 (1.82%)	$y = -3.43 \times 10^{-2} + 2.94 \times 10^{-2} x$ (99.80%, 5.78×10^{-2}) (0/15)	3.92% (n=11)	$y = -5.62 \times 10^{-3} + 1.00 x$ (99.80%, 1.96)	3.73	7.33
DiNP	2 factors (Factor 1: DiNP) Non-negativity constraint in the three modes Explained variance: 99.55% CORCONDIA: 100%	$t_{R,rel}$ = -[a] 57 (29.84%) 127 (9.80%) 149 (100%) 167 (9.44%) 275 (0.58%) 293 (12.30%)	$y = -1.76 \times 10^{-2} + 4.75 \times 10^{-4} x + 3.40 \times 10^{-8} x^2$ (99.83%, 4.80×10^{-2}) (0/15)	2.45% (n=13)	$y = 4.96 \times 10^{-1} + 1.00 x$ (99.85%, 68.68)	133.5	262.2

[a] It is not possible to establish a retention time for DiNP.

[b] Mean of the absolute value of the relative error in calibration calculated excluding the samples with predicted concentration lower than CCβ.

Table 4 Results obtained in the two-way ANOVA for the evaluation of the effect of the Soxhlet position and the fritted funnel on the recovery of the analytes. Variance due to the effect of: the Soxhlet position (σ_τ^2), the fritted funnel (σ_β^2), the interaction between both factors ($\sigma_{\tau\beta}^2$), the error (σ_0^2) and the total variance (σ_{TOTAL}^2) together with their corresponding standard deviations. The percentages of the total variance of the response due to each effect for every analyte are in brackets.

Analyte	Variance					Standard deviation (%)				
	σ_τ^2	σ_β^2	$\sigma_{\tau\beta}^2$	σ_0^2	σ_{TOTAL}^2	σ_τ	σ_β	$\sigma_{\tau\beta}$	σ_0	σ_{TOTAL}
BHT	43.81	7.54	4.24	5.76	61.35	6.62	2.75	2.06	2.40	7.83

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	(71.41%)	(12.29%)	(6.91%)	(9.39%)						
BP	447.85 (88.07%)	8.53 (1.68%)	41.24 (8.11%)	10.92 (2.15%)	508.54	21.16	2.92	6.42	3.30	22.55
DiBP	41.11 (39.87%)	22.91 (22.22%)	37.84 (36.70%)	1.25 (1.21%)	103.11	6.41	4.79	6.15	1.12	10.15
DEHA	93.15 (40.52%)	17.09 (7.43%)	119.38 (51.92%)	0.29 (0.13%)	229.91	9.65	4.13	10.93	0.54	15.16
DiNP	48.22 (26.46%)	34.88 (19.14%)	98.50 (54.05%)	0.63 (0.35%)	182.23	6.94	5.91	9.92	0.79	13.50

Table 5 PARAFAC models estimated with the data from the two-way ANOVA for the selection of the optimum mode of agitation, identification of every analyte (relative retention time and the relative abundances for each diagnostic ion in brackets) and parameters of the calibration models estimated for the five analytes from the two calibration sets.

			Regression model "standardized sample loadings versus true concentration"			
Analyte	PARAFAC model	Identification	Model for the first calibration set (R^2, s_{yx}) (Outliers/standards)	Error (%)[b]	Model for the second calibration set (R^2, s_{yx}) (Outliers/standards)	Error (%)[b]
BHT	1 factor Unconstrained model Explained variance: 99.25%	$t_{R,rel}$ = 0.80891 (6.94%) 145 (11.78%) 177 (8.00%) 205 (100%) 220 (23.89%)	$y = -3.09 \times 10^{-2} + 2.67 \times 10^{-2} x$ (99.87%, 3.54×10^{-2}) (1/15)	2.59% (n=12)	$y = -5.98 \times 10^{-2} + 1.96 \times 10^{-2} x$ (99.59%, 4.39×10^{-2}) (0/15)	3.77% (n=11)
BP	1 factor Unconstrained model Explained variance: 86.86%	$t_{R,rel}$ = 0.88851 (18.81%) 77 (57.77%) 105 (100%) 152 (4.09%) 182 (57.37%)	$y = -3.75 \times 10^{-2} + 7.20 \times 10^{-3} x + 2.78 \times 10^{-4} x^2$ (99.53%, 7.16×10^{-2}) (1/15)	6.38% (n=10)	$y = 7.78 \times 10^{-3} - 3.46 \times 10^{-3} x + 2.78 \times 10^{-4} x^2$ (99.42%, 6.52×10^{-2}) (0/15)	4.70% (n=9)

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DiBP-d_4	2 factors (Factor 2: DiBP-d_4) Non-negativity constraint in modes 1 and 2 Explained variance: 98.70% CORCONDIA: 96%	$t_{R,rel}$ = 1.000 80 (6.29%) 153 (100%) 171 (2.75%) 209 (2.33%) 227 (5.17%)	Internal standard		Internal standard	
DiBP	2 factors (Factor 1: DiBP) Non-negativity constraint in modes 1 and 2 Explained variance: 98.70% CORCONDIA: 96%	$t_{R,rel}$ = 1.001 104 (7.72%) 149 (100%) 167 (2.81%) 205 (1.44%) 223 (5.64%)	$y = 2.36 \times 10^{-1} + 1.53 \times 10^{-2} x$ (99.32%, 4.89 × 10^{-2}) (0/15)	4.04% (n=14)	$y = 1.66 \times 10^{-1} + 1.16 \times 10^{-2} x$ (99.78%, 2.12 × 10^{-2}) (1/15)	2.89% (n=13)
DEHA	1 factor Unconstrained model Explained variance: 98.25%	$t_{R,rel}$ = 1.281 112 (33.24%) 129 (100%) 147 (16.35%) 241 (4.36%) 259 (1.83%)	$y = -2.05 \times 10^{-2} + 2.35 \times 10^{-2} x$ (99.78%, 4.91 × 10^{-2}) (0/15)	4.13% (n=11)	$y = -5.43 \times 10^{-2} + 1.39 \times 10^{-2} x + 3.74 \times 10^{-5} x^2$ (99.59%, 5.34 × 10^{-2}) (0/15)	4.86% (n=10)
DiNP	2 factors (Factor 2: DiNP) Non-negativity constraint in the three modes Explained variance: 99.72% CORCONDIA: 100%	$t_{R,rel}$ = -[a] 57 (31.44%) 127 (9.85%) 149 (100%) 167 (9.63%) 275 (0.60%) 293 (12.57%)	$y = -8.14 \times 10^{-3} + 3.75 \times 10^{-4} x + 2.39 \times 10^{-8} x^2$ (99.82%, 3.84 × 10^{-2}) (0/15)	2.54% (n=13)	$y = -5.65 \times 10^{-2} + 3.49 \times 10^{-4} x + 2.42 \times 10^{-8} x^2$ (99.83%, 3.46 × 10^{-2}) (1/15)	2.44% (n=12)

[a] It is not possible to establish a retention time for DiNP.
[b] Mean of the absolute value of the relative error in calibration calculated excluding the samples with predicted concentration lower than CCβ.

Table 6 Values of the average recovery rates and the coefficient of variation obtained with the modes of agitation 1, 2, 3 and 4 for every analyte.

Analyte	Average recovery rates (%) (n = 8)				Coefficient of variation (%)			
	Factor level[a]				Factor level[a]			
	Mode 1	Mode 2	Mode 3	Mode 4	Mode1	Mode 2	Mode 3	Mode 4
BHT	70.71	41.15	62.92	79.14	5.56	19.77	14.25	55.95

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BP	110.80	120.18	79.98	104.29	4.24	7.02	15.34	7.46
DiBP	48.34	73.62	36.24	36.66	13.43	7.63	23.91	21.76
DEHA	12.78	28.52	14.16	13.17	17.10	23.66	37.94	21.19
DiNP	44.40	53.36	58.26	58.94	3.67	11.65	7.96	15.39

[a] Levels of the factor (mode of agitation): mode 1 (an orbital shaker at 180 oscillations min^{-1} for 5 min together with manual stirring for 20 s), mode 2 (a vortex mixer working for 2 min), mode 3 (a rocking mixer for 15 min) and mode 4 (a magnetic stirrer at 1500 rpm for 15 min) in each extraction step.

Table 7 Results obtained in the second two-way ANOVA performed for the selection of the optimum mode of agitation. Variance due to the effect of: the mode of agitation (σ_τ^2), the fritted funnel (σ_β^2), the interaction between them ($\sigma_{\tau\beta}^2$), the error (σ_0^2) and the total variance (σ_{TOTAL}^2) together with the corresponding standard deviations. The percentages of the total variance of the response due to each effect are in brackets. Values of the average recovery rates and coefficient of variation obtained with the mode of agitation 1, 4, 5 and 6 for every analyte.

Analyte	Variance					Standard deviation (%)					Average recovery rates (%) (n = 8)				Coefficient of variation (%)			
	σ_τ^2	σ_β^2	$\sigma_{\tau\beta}^2$	σ_0^2	σ_{TOT}^2	σ_τ	σ_β	$\sigma_{\tau\beta}$	σ_0	σ_{TOT}	Factor level[a]				Factor level[a]			
											Mode 1	Mode 4	Mode 5	Mode 6	Mode 1	Mode 4	Mode 5	Mode 6
BHT	59.17	176.60	464.26	50.81	750.84	7.69	13.29	21.55	7.13	27.40	70.46	78.75	69.31	59.01	5.50	55.78	6.19	10.63
	(7.88 %)	(23.52 %)	(61.83 %)	(6.77 %)														
BP	610.09	4.06	9.69	31.58	655.42	24.7	2.02	3.11	5.62	25.60	110.75	103.80	159.31	120.52	4.26	7.53	1.40	7.28
	(93.08 %)	(0.62 %)	(1.48 %)	(4.82 %)														
DiBP	176.80	11.12	41.16	2.55	231.63	13.30	3.33	6.42	1.60	15.22	48.24	36.86	68.97	50.11	13.43	21.35	9.12	6.53
	(76.33 %)	(4.80 %)	(17.77 %)	(1.10 %)														
DEHA	147.64	11.42	17.59	0.52	177.17	12.15	3.38	4.19	0.72	13.31	12.83	13.19	20.91	38.78	17.07	21.29	15.34	20.54
	(83.33 %)	(6.45 %)	(9.93 %)	(0.29 %)														
DiNP	111.61	17.55	21.39	2.76	153.31	10.56	4.19	4.63	1.66	12.38	44.37	58.82	49.18	68.21	3.58	15.26	8.89	7.19

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(72.80 %)	(11.45 %)	(13.95 %)	(1.80 %)

[a] Levels of the factor (mode of agitation): mode 1 (an orbital shaker at 180 oscillations min^{-1} for 5 min together with manual stirring for 20 s), mode 4 (a magnetic stirrer at 1500 rpm for 15 min), mode 5 (an orbital shaker at 180 oscillations min^{-1} for 15 min together with manual stirring for 20 s) and mode 6 (a magnetic stirrer at 1500 rpm for 7 min 30 s stopping each 30 s and restarting after 5 s) in each extraction step.

Table 8 PARAFAC models estimated with the data from the study of the reuse of Tenax, identification of every analyte (relative retention time and the relative abundances for each diagnostic ion in brackets) and parameters of the calibration model and of the accuracy line.

			Calibration model	Accuracy line		
Analyte	PARAFAC model	Identification	Model (R^2, s_{yx}) (Outliers/standards)	Model (R^2, s_{yx})	p-value for the intercept	p-value for the slope
BHT	1 factor Unconstrained model Explained variance: 99.60%	$t_{R,rel}$ = 0.807 91 (6.33%) 145 (11.30%) 177 (7.78%) 205 (100%) 220 (24.06%)	$y = 1.16 \times 10^{-2} + 7.24 \times 10^{-3} x + 4.67 \times 10^{-4} x^2$ (99.92%, 5.40×10^{-2}) (1/15)	$y = 3.73 \times 10^{-1} + 0.99 x$ (99.86%, 1.35)	0.53	0.59
BP	1 factor Unconstrained model Explained variance: 79.09%	$t_{R,rel}$ = 0.883 51 (18.21%) 77 (57.28%) 105 (100%) 152 (4.31%) 182 (60.95%)	$y = -1.35 \times 10^{-1} + 2.18 \times 10^{-2} x + 3.70 \times 10^{-4} x^2$ (99.14%, 1.67×10^{-1}) (1/15)	$y = 3.48 \times 10^{-1} + 0.99 x$ (98.57%, 3.86)	0.84	0.80
DiBP-d_4	2 factors (Factor 2: DiBP-d_4) Non-negativity constraint in modes 1 and 2 Explained variance: 98.58% CORCONDIA: 87%	$t_{R,rel}$ = 1.000 80 (6.21%) 153 (100%) 171 (2.74%) 209 (1.89%) 227 (5.18%)	Internal standard	Internal standard		
DiBP	2 factors (Factor 1: DiBP) Non-negativity constraint in modes 1 and 2 Explained variance: 98.58% CORCONDIA: 87%	$t_{R,rel}$ = 1.001 104 (8.17%) 149 (100%) 167 (2.78%) 205 (1.44%) 223 (5.55%)	$y = 1.51 \times 10^{-1} + 2.16 \times 10^{-2} x$ (99.50%, 5.92×10^{-2}) (0/15)	$y = -1.38 \times 10^{-2} + 1.00 x$ (99.50%, 2.74)	0.99	0.91

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DEHA	1 factor Unconstrained model Explained variance: 98.75%	$t_{R,rel}$ = 1.280 112 (32.75%) 129 (100%) 147 (15.58%) 241 (4.46%) 259 (1.78%)	$y = -1.28 \times 10^{-1} + 4.37 \times 10^{-2} x$ (99.73%, 9.72×10^{-2}) (1/15)	$y = 2.24 \times 10^{-3} + 1.00 x$ (99.73%, 2.22)	1.00	0.98
DiNP	2 factors (Factor 1: DiNP) Non-negativity constraint in the three modes Explained variance: 99.50% CORCONDIA: 100%	$t_{R,rel}$ = -[a] 57 (28.32%) 127 (9.72%) 149 (100%) 167 (9.69%) 275 (0.60%) 293 (12.97%)	$y = -1.73 \times 10^{-2} + 5.20 \times 10^{-4} x + 4.18 \times 10^{-8} x^2$ (99.95%, 3.06×10^{-2}) (1/15)	$y = 3.07 \times 10^{-1} + 1.00 x$ (99.96%, 37.73)	0.99	0.97

[a] It is not possible to establish a retention time for DiNP.

Table 9 Results of the paired sample t-test performed to compare the predicted concentration of each analyte obtained in the Tenax blanks (D-A) and the spiked Tenax samples (C-B, E-B and E-C) with the data from the study of the reuse of Tenax for the two concentration levels considered.

Analyte		Concentration level 1				Concentration level 2			
		D-A[a]	C-B[b]	E-B[c]	E-C[d]	D-A[a]	C-B[b]	E-B[c]	E-C[d]
BHT	Average (n = 8)	-7.30	-7.72	-7.29	0.43	-22.09	-9.37	-6.75	2.63
	Standard deviation	0.39	2.42	2.62	2.59	3.46	1.37	8.77	8.16
	p-value	2.47×10^{-10}	4.20×10^{-5}	1.00×10^{-4}	0.66	3.94×10^{-7}	2.42×10^{-7}	0.07	0.39
BP	Average (n = 8)	-2.01	-1.91	-4.62	-2.71	-0.46	-5.04	-7.94	-2.90
	Standard deviation	0.58	0.47	1.19	1.20	0.80	1.58	2.42	1.38
	p-value	2.46×10^{-5}	9.04×10^{-6}	3.80×10^{-4}	3.07×10^{-1}	0.14	4.15×10^{-5}	3.52×10^{-5}	5.70×10^{-4}
DiBP	Average (n = 8)	-10.30	1.63	0.84	-0.80	-1.98	-8.39	5.77	14.15
	Standard deviation	2.84	1.97	4.23	5.06	2.78	1.28	3.75	3.72
	p-value	1.80×10^{-5}	0.05	0.59	0.67	0.08	3.29×10^{-7}	3.36×10^{-3}	1.31×10^{-5}
DEHA	Average (n = 8)	-1.25×10^{-3}	-0.45	-4.03	-3.68	-0.12	-7.10	6.70	13.80
	Standard deviation	0.08	1.88	0.58	1.96	0.09	3.05	1.68	3.06
	p-value	0.96	0.62	2.22×10^{-7}	1.12×10^{-3}	6.24×10^{-3}	3.10×10^{-4}	9.63×10^{-6}	4.26×10^{-6}
DiNP	Average (n = 8)	-0.99	-84.50	-95.66	-11.16	4.69	-125.38	-16.19	109.19
	Standard deviation	11.62	44.40	98.54	102.75	8.35	132.25	150.19	189.49

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p-value	0.82	1.03×10^{-3}	0.03	0.77	0.16	0.03	0.77	0.15

[a] D: Blanks prepared with Tenax cleaned twice, A: Blanks prepared with Tenax cleaned once
[b] C: Spiked samples prepared with Tenax cleaned twice, B: Spiked samples prepared with Tenax cleaned once
[c] E: Spiked samples prepared with Tenax cleaned three times, B: Spiked samples prepared with Tenax cleaned once
[d] E: Spiked samples prepared with Tenax cleaned three times, C: Spiked samples prepared with Tenax cleaned twice

Table 10 PARAFAC models estimated with the data from the migration study and identification of every analyte (relative retention time and the relative abundances for each diagnostic ion in brackets). Parameters of the calibration model and of the accuracy line. CCα and CCβ at $x_0 = 0$ ($\alpha = \beta = 0.05$) and average concentration of each analyte in the Tenax blank and in the printed paper sample (s, standard deviation).

			Calibration model	Accuracy line	CCα (x = 0) (µg L^{-1})	CCβ (x = 0) (µg L^{-1})	Average concentration (µg L^{-1})	
Analyte	PARAFAC model	Identification	Model (R^2, s_{yx}) (Outliers/standards)	Model (R^2, s_{yx})			Blanks (n = 2)	Paper sample (n = 5)
BHT	1 factor Unconstrained model Explained variance: 99.80%	$t_{R,rel}$ = 0.80791 (6.33%) 145 (11.57%) 177 (7.67%) 205 (100%) 220 (24.04%)	$y = 4.86 \times 10^{-2} + 4.07 \times 10^{-4} x + 2.41 \times 10^{-3} x^2$ (99.95%, 6.22×10^{-2}) (1/7)	$y = 7.31 \times 10^{-1} + 0.98 x$ (99.96%, 4.09×10^{-1})	1.20	2.28	10.35 s = 1.70	12.91 s = 1.89
BP	1 factor Unconstrained model Explained variance: 94.67%	$t_{R,rel}$ = 0.88551 (18.91%) 77 (57.07%) 105 (100%) 152 (3.92%) 182 (60.38%)	$y = 2.59 \times 10^{-2} - 2.07 \times 10^{-2} x + 3.33 \times 10^{-3} x^2$ (99.97%, 2.81×10^{-2}) (1/7)	$y = 3.06 + 0.88 x$ (98.01%, 1.96)	5.54	10.57	5.80 s = 0.19	7.57 s = 1.59
DiBP-d_4	2 factors (Factor 2: DiBP-d_4) Non-negativity constraint in modes 1 and 2 Explained variance: 99.05% CORCONDIA: 90%	$t_{R,rel}$ = 1.00080 (6.33%) 153 (100%) 171 (2.81%) 209 (1.41%) 227 (5.44%)	Internal standard	Internal standard				

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DiBP	2 factors (Factor 1: DiBP) Non-negativity constraint in modes 1 and 2 Explained variance: 99.05% CORCONDIA: 90%	$t_{R,rel}$ = 1.000 104 (8.35%) 149 (100%) 167 (2.82%) 205 (1.41%) 223 (5.53%)	$y = 3.01 \times 10^{-1} + 4.14 \times 10^{-2} x$ (99.67%, 6.61×10^{-2}) (0/7)	$y = -4.04 \times 10^{-3} + 1.00 x$ (99.67%, 1.60)	4.10	7.87	22.12 s = 2.24	12.42 s = 4.75
DEHA	1 factor Unconstrained model Explained variance: 98.99%	$t_{R,rel}$ = 1.280 112 (31.84%) 129 (100%) 147 (17.42%) 241 (4.55%) 259 (1.62%)	$y = -1.12 \times 10^{-1} + 1.14 \times 10^{-1} x$ (99.85%, 7.90×10^{-2}) (0/7)	$y = -3.08 \times 10^{-3} + 1.00 x$ (99.85%, 6.92×10^{-1})	1.58	3.04	1.19 s = 0.04	2.41 s = 0.73
DiNP	2 factors (Factor 1: DiNP) Non-negativity constraint in the three modes Explained variance: 99.46% CORCONDIA: 100%	$t_{R,rel}$ = -[a] 57 (29.81%) 127 (9.54%) 149 (100%) 167 (9.50%) 275 (0.56%) 293 (12.70%)	$y = -3.89 \times 10^{-2} + 1.48 \times 10^{-3} x + 1.21 \times 10^{-7} x^2$ (99.94%, 5.03×10^{-2}) (0/7)	$y = -4.12 \times 10^{-2} + 1.00 x$ (99.94%, 27.49)	65.00	124.8	0	0

[a] It is not possible to establish a retention time for DiNP.

Highlights

- The extensive cleaning of Tenax by Soxhlet affects its adsorption capability
- Tenax cannot be reused in the multiresidue analysis of some plasticizers and BP
- Tenax can be reused in the analysis of DiBP and/or DEHA in certain circumstances
- BHT was contained in the Tenax blank and has migrated from a printed paper sample
- PARAFAC succeeds in identifying unequivocally and quantifying finger-peak analytes

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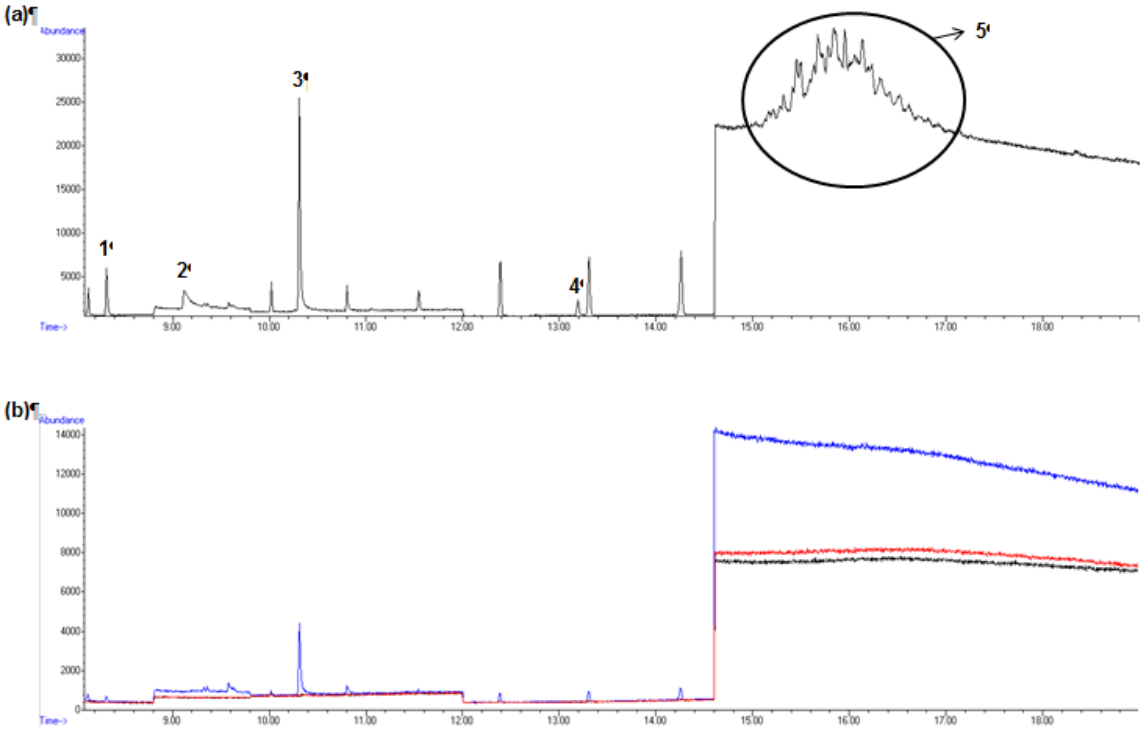

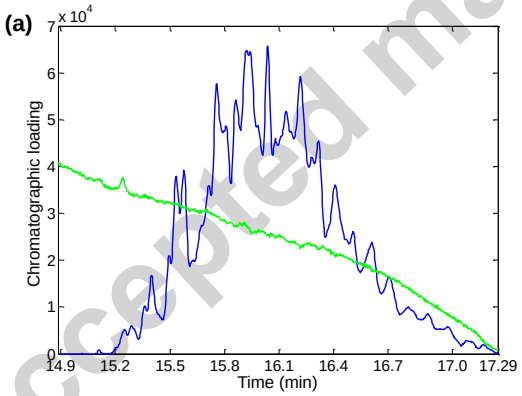

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Fig.2 a

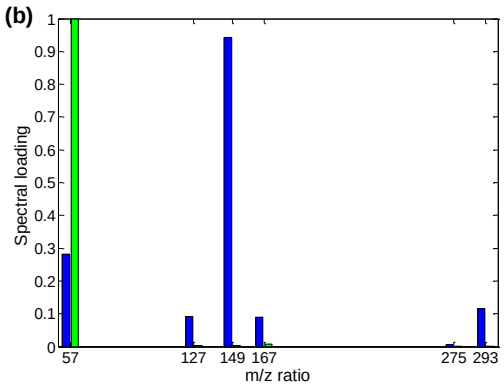

Fig.2 b

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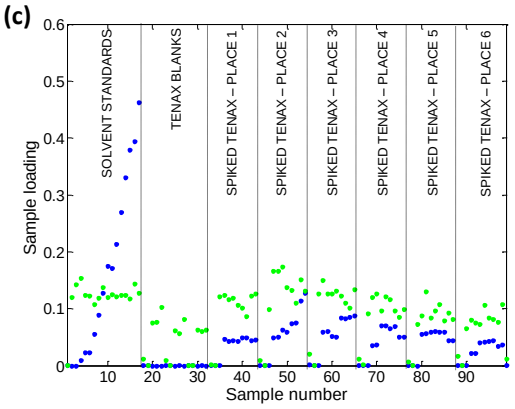

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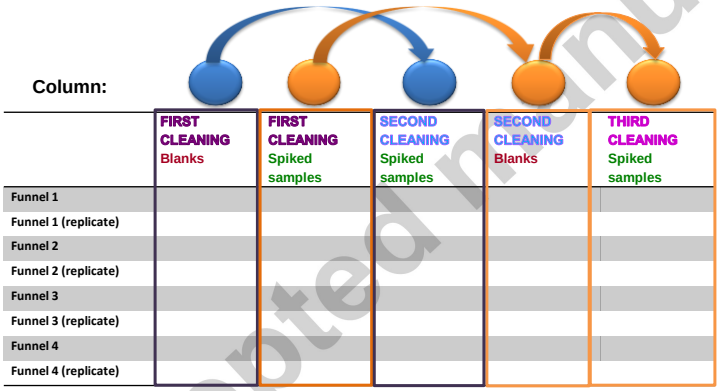

Fig. 3

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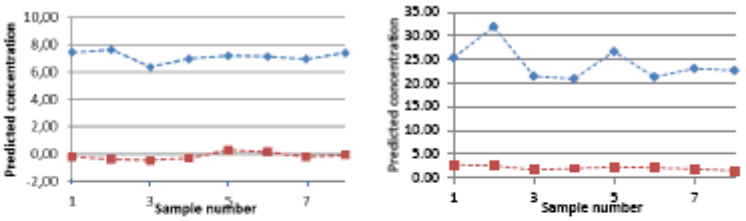
BHT



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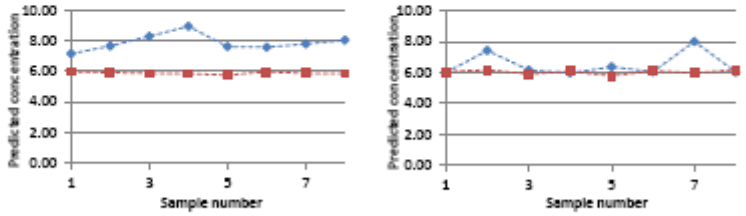

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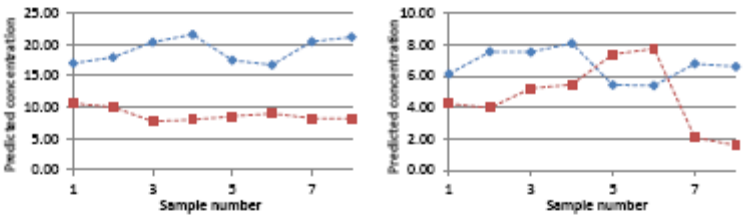

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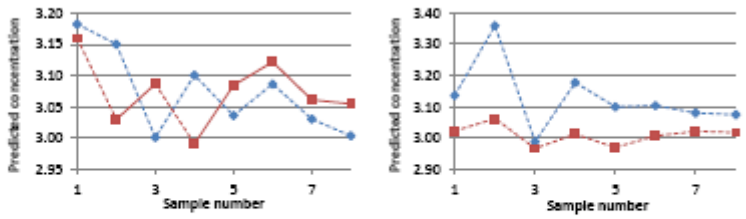
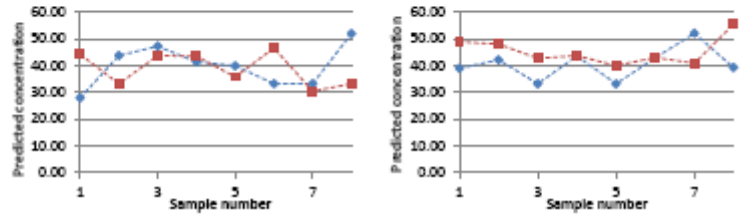


DiNP



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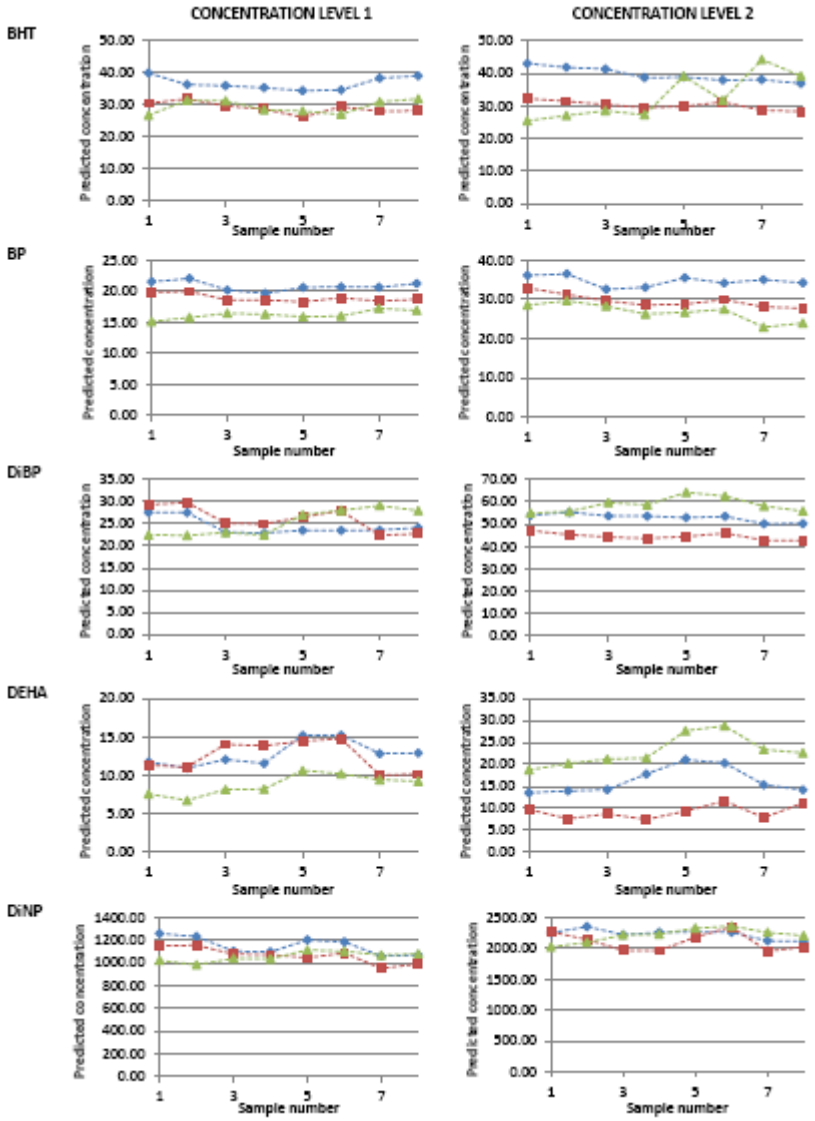

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