# Determination of polymer additive residues that migrate from coffee capsules by means of stir bar sorptive extraction-gas chromatography-mass spectrometry and PARAFAC decomposition

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## ABSTRACT

This paper reports on the difficulties encountered when developing an analytical method for ultra-trace determination, in a complex matrix, of plastic additive residues which are ubiquitous in the laboratory. The simultaneous qualitative and quantitative determination of an antioxidant (2,6-di-tert-butyl-4-methyl-phenol, BHT), an UV stabilizer (benzophenone, BP), and a plasticizer (diisobutyl phthalate, DiBP), released from plastic capsules is carried out in coffee by means of GC–MS and parallel factor analysis decomposition. Stir bar sorptive extraction is used to extract and concentrate the analytes. Coffee samples are prepared with Milli-Q water, which contains residues of the target compounds, which can be significant for ultra-trace analysis and should be subtracted. In addition, matrix effect exits in coffee, so standard addition method is used. The residue concentrations released from the coffee capsules into the solid coffee are around 3, 1, and 12 μg kg$^{-1}$ of BHT, BP and DiBP, respectively.

## 1. Introduction

One of the most widely consumed beverages in the world is coffee. Coffee can be brewed from instant coffee or from ground coffee in Italian or French coffee makers, but nowadays the use of coffee machines to make coffee at home is growing. In this case, the coffee can be brewed from metallic or plastic pre-portioned coffee capsules containing different types of coffee. But these packaging materials, which are in contact with foodstuffs, are not inert by their design. Food comes into contact with many materials during its production, processing, storage and preparation, before its eventual consumption. Food Contact Materials (FCMs) are defined by the European Food Safety Authority (EFSA) as "all materials and articles intended to come into contact with food". In the European Union is facilitated a series of legal requirements and controls to ensure the safety of FCMs. Regulation (EC) No 1935/2004 estates that FCMs must be sufficiently inert so as not to transfer substances into food in quantities that could endanger human health (Wrona & Nerín, 2020). Different materials and articles, such as active and intelligent materials, adhesives, ceramics, metals and alloys, paper and board, plastics, printing inks, between other materials, are covered by specific measures. Commission Regulation (EU) No 10/2011 sets rules on the composition of plastic FCMs and establishes the specific migration limits (SMLs) as "the maximum permitted amount of a given substance released from a material or article into food or food simulants". These limits are established according to toxicological evaluations carried out by EFSA.

This work studies the determination of some polymer additives present on food contact plastic materials such as: an antioxidant (2,6-di-tert-butyl-4-methyl-phenol, BHT), an UV stabilizer (benzophenone, BP), and a plasticizer (diisobutyl phthalate, DiBP) (De Toni et al., 2017; Fasano, Bono-Blay, Cirillo, Montouri, & Lacorte, 2012). The SMLs are fixed at 3 and 0.6 mg kg$^{-1}$ for BHT and BP, respectively, which is

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expressed in mg substance per kg food. DiBP is non-listed substance, which means that it is not authorized for making food contact plastics. In this case, the limit of 0.010 mg kg$^{-1}$ applies, which is the limit established in the Commission Regulation (EU) 10/2011 for functional barriers. These compounds pose a risk to human health. Phthalates and plasticizers, as well as BHT (Alofe et al., 2019; Al-Shabib et al., 2017), are endocrine disruptors which adversely affect hormonal function (De Toni et al., 2017; Holmes, 2013; Ventrice, Ventrice, Russo, & De Sarro, 2013). In addition, DiBP has been classified as carcinogenic, mutagenic or toxic substance to reproduction (category 1B) in Commission Regulation (EC) No 790/2009 and as very dangerous substance in REACH (Registration, Evaluation, Authorization and Restriction of Chemical substances) (Ventrice et al., 2013).

These compounds are present in coffee capsules which are made of plastic. There are different methods to extract the compounds which migrate from coffee capsules into coffee when it is desired to carry out their analytical determination. Solid-phase extraction (SPE) cartridges are widely used in the literature to extract the compounds (Di Bella, Potortì, Lo Turco, Saitta, & Dugo, 2014; Mohamed & Ammar, 2008; Wu, Pan, Ma, Wang, & Zhang, 2014). On the other hand, the liquid-liquid extractions with water/dichloromethane (De Toni et al., 2017) or hexane (Guo et al., 2012; Rubio, Valverde-Som, Sarabia, & Ortiz, 2019) have been used as alternative to avoid the SPE. Then, gas chromatography-mass spectrometry (GC–MS) is used in all of these papers as instrumental technique to separate, identify and quantify the compounds. Other extraction methods, such as salting out liquid-liquid extraction (SALLE), have been used coupled to liquid chromatography (Otoukesh, Vera, Wrona, Nerin, & Es'haghi, 2020).

However, other technique to extract the compounds highly efficiently and more environment friendly is stir bar sorptive extraction (SBSE) which is a technique of sample preparation that includes extraction and concentration of the analytes in a single step. This technique uses a polydimethylsiloxane (PDMS) layer as sorbent phase, avoiding the use of large volumes of solvents. Although it is based on the same principles as solid-phase microextraction (SPME), SBSE exhibits much higher sensitivity, due to the greater amount of PDMS in the coating film of stir bars compared to SPME fibres. For that reason, this extraction technique has been successfully applied to monitor traces or ultra-traces around parts per trillion (Nogueira, 2015). SBSE has been used to extract different polymer additives in other matrices (Cacho, Campillo, Viñas, & Hernández-Córdoba, 2012; Farajzadeh, Sorouraddin, & Mogaddam, 2015; Guart, Calabuig, Lacorte, & Borrell, 2014) and to determinate another compounds in coffee (Bicchi, Iori, Rubiolo, & Sandra, 2002; Ridgway, Lalljie, & Smith, 2010).

On the other hand, phthalates, which are ubiquitous in the laboratory (Oca, Rubio, Sarabia, & Ortiz, 2016), and benzophenone have been analysed in Milli-Q water samples (Ivancev-Tumbas, Bogunovic, Cesen, Tubic, & Heath, 2019; López-Roldán, López de Alda, & Barceló, 2004). Milli-Q water is subject of study in this work to ensure if these compounds migrate from coffee capsules and that they are not released from the water purification system, which is made of plastic materials.

Therefore, in this work, some polymer additives present in plastic materials (BHT, BP, and DiBP) are determined by SBSE-GC–MS in coffee brewed from coffee capsules and in Milli-Q water. GC–MS data can be arranged in a three-way array (chromatographic mode, spectra mode and sample mode) which can be analysed using parallel factor analysis (PARAFAC) (Bro & Kiers, 2003; Bro, 1997). PARAFAC decomposition methods have been used to know if a coeluent that shares *m/z* ratios with the analytes of interest is present, to avoid its interference and to identify unequivocally the target compounds (Ortiz et al., 2015, 2020; Ortiz & Sarabia, 2007).

## 2. Material and methods

### 2.1. Chemicals

Benzophenone (BP, CAS no. 119-61-9, purified by sublimation, $\geq$ 99 % purity), 2,6-di-tert-butyl-4-methyl-phenol (BHT, CAS no. 128-37-0, $\geq$ 99 % purity), diisobutyl phthalate (DiBP, CAS no. 84-69-5, 99 % purity), and diisobutyl phthalate-3,4,5,6-d$_4$ (DiBP-d$_4$, CAS no. 358730-88-8, 99.7 % purity), used as internal standard (IS), are purchased from Sigma-Aldrich (Steinheim, Germany).

Acetone (CAS no. 67-64-1), methanol (CAS no. 67-56-1) and n-hexane (CAS no. 110-54-3), for liquid chromatography Lichrosolv® are from Merck KGaA (Darmstadt, Germany). A Milli-Q gradient A10 water purification system from Millipore (Bedford, MA, USA) is used to obtain Milli-Q water. Helium (99.999 % purity, ALPHAGAZ™1, Air Liquide, Madrid, Spain) is used as the carrier gas.

### 2.2. Standard solutions

Stock solutions of BHT at 4600 mg L$^{-1}$, of BP at 1300 mg L$^{-1}$, of DiBP-d$_4$ at 360 mg L$^{-1}$ and of DiBP at 4000 mg L$^{-1}$ are prepared individually in methanol and are stored in sealed crimp vials at 4 °C and protected from light. The vial weight is controlled under gravimetric control to verify that the solvent has not evaporated.

The first intermediate solutions are prepared from the former ones by dilution with methanol. The second intermediate solutions are prepared from Milli-Q water, which is the final solvent. Two intermediate solutions are necessary to ensure the final concentration of ng L$^{-1}$. All intermediate solutions are prepared daily.

Fourteen reference standards, to estimate the tolerance intervals for relative time and relative ion abundances, together with spiked Milli-Q water solutions are prepared from the intermediate solutions in 10 mL volumetric flasks. Eleven of them contain the analytes at different concentration ranges (0−1350 ng L$^{-1}$ of BHT and BP, 0−700 ng L$^{-1}$ of DiBP-d$_4$ and 0−10000 ng L$^{-1}$ of DiBP) and the IS, DiBP-d$_4$, at a fixed concentration (250 ng L$^{-1}$). The three remaining standards contain the analytes at a fixed concentration (at an intermediate level) and the IS at three different concentration levels (100, 500 and 700 ng L$^{-1}$). The concentration ranges for the spiked Milli-Q water samples are 0−1250 ng L$^{-1}$ of BHT and BP, 0−500 ng L$^{-1}$ of DiBP-d$_4$ and 0−5000 ng L$^{-1}$ of DiBP.

### 2.3. Coffee samples

Coffee capsules of a given medium roast decaf coffee from the same batch are purchased from a local market (Burgos, Spain). Capsules are made of mixed plastics and a small amount of aluminium at the bottom. The 6 g of coffee contained in a capsule is used to obtain each spiked coffee sample. Each portion is placed in a 100 mL beaker containing 50 mL of boiling Milli-Q water to aid leaching, stirred with a rod and then left to cool at room temperature. Spiked coffee samples are prepared by adding appropriate volumes of the intermediate solutions in 10 mL volumetric flask and making up the volume with the brewed coffee.

Two different concentration ranges for the target plastic additives are studied; the analyses are made on two different days: day 1 and 2. The concentration ranges of the spiked coffee samples for day 1 are 0−1250 ng L$^{-1}$ of BHT and BP, 0−500 ng L$^{-1}$ of DiBP-d$_4$ and 0−5000 ng L$^{-1}$ of DiBP, and, for day 2, 0−2500 ng L$^{-1}$ of BHT, 0−15000 ng L$^{-1}$ of BP, 0−1500 ng L$^{-1}$ of DiBP-d$_4$ and 0−15000 ng L$^{-1}$ of DiBP. All spiked samples are prepared daily.

### 2.4. Instrumentation

Stir bars with 10 mm × 0.5 mm polydimenthylsiloxane (PDMS) coating film, which are commercially available as Gerstel Twisters® (Mülheiman der Ruhr, Germany), are used. A tube conditioner TC 2 and

the controller C200 from GERSTEL GmbH & Co. KG (Mülheiman der Ruhr, Germany) are used for the conditioning of the stir bars. A magnetic stirrer GERSTEL 20 Position Twister Stir Plate (Mülheiman der Ruhr, Germany) is also used for sample extraction.

All chromatographic separations are performed using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrometer detector with a single quadrupole mass analyser (Agilent Technologies, Santa Clara, CA, USA). The injection device is an automated thermal desorption unit (TDU) connected to a programmed temperature vaporizer (PTV) injector CIS 4 from GERSTEL GmbH & Co. KG (Mülheiman der Ruhr, Germany), both with universal Peltier cooling modules, and coupled to the MultiPurpose Sampler MPS2XL. The PTV is equipped with a deactivated empty glass liner with baffles. The analytical column is a capillary column coated with a (5%-phenyl)-methylpolysiloxane stationary phase (Agilent HP-5MS Ultra Inert column; 30 m × 0.25 mm inner diameter ×0.25 μm film thickness).

### 2.5. SBSE procedure

The plastic consumables are avoided as far as possible and the laboratory glassware used was thoroughly cleaned. Thus, n-hexane, acetone, and methanol, in that order, are used in the final cleaning prior to use throughout the experimental work.

The stir bars are cleaned-up and conditioned before each extraction. In this process, the stir bars are fit into empty thermal desorption system tubes; tube conditioning is then performed in the tube conditioner TC 2 at high temperatures under a flow of inert gas. In this work, two consecutive thermal conditioning programs are applied with a constant flow of nitrogen at a pressure of 400 kPa: i) 30 min at 275 °C, then cool down until 100 °C; ii) 5 min at 100 °C and then the temperature is increased at 10 °C min$^{-1}$ to 250 °C, which is held for 30 min. Then, that temperature is ramped again at 10 °C min$^{-1}$ to 300 °C, which is held for 60 min, and finally, cool down to 80 °C. Following conditioning, the tubes are allowed to cool to room temperature for 30 min and the stir bars are then ready to use.

10 mL of each solution is placed into a 50 mL Erlenmeyer flask with a stir bar and extracted for 4 h at a stirring speed of 750 rpm. Then, the stir bar is collected using a magnetic stirring bar retriever, dipped briefly in Milli-Q water, dried with a delicate task wiper (Kimwipes®, from Sigma-Aldrich), placed in a TDU liner, thermally desorbed and analysed by GC–MS.

### 2.6. GC–MS experimental conditions

The thermal desorption is performed by maintaining the TDU at 50 °C for 0.1 min, with 0.3 min of delay time, and increasing the temperature at 200 °C min$^{-1}$ to 250 °C, which is held for 10 min. The analytes are transferred at 260 °C for 0.3 min of vent time and focused in the PTV inlet at 30 °C. The PTV inlet operates in the cold splitless mode. Once focusing is completed, the analytes are transferred into the capillary column. The inlet temperature is ramped at 4.16 °C s$^{-1}$ up to 275 °C, which is held for 15 min. The septum purge flow rate is 3 mL min$^{-1}$ while the purge flow rate through the split vent is fixed at 40 mL min$^{-1}$ (vent pressure 93.1 kPa) for 0.3 min and the purge to split vent at 30 mL min$^{-1}$ for 9 min.

Subsequently, the column oven temperature is maintained at 40 °C for 0.6 min and then is increased at 20 °C min$^{-1}$ to 250 °C, which is held for 1 min, and next is ramped again at 10 °C min$^{-1}$ to 290 °C, which is held for 3 min. The run time is 19.1 min and a post-run step is carried out at 300 °C for 4 min. Flow rate of the carrier gas is set at 1.3 mL min$^{-1}$ and initial pressure is set at 69.8 kPa.

The mass spectrometer conditions are as follows: the transfer line temperature is set at 300 °C, the ion source at 230 °C and the quadrupole at 150 °C. The MS operates in the electron impact (EI) ionization mode at 70 eV. Data are acquired in single ion monitoring (SIM) mode, after a solvent delay of 8 min, using three acquisition windows: i) for BHT peak

(start time: 8 min, ion dwell time: 30 ms), the diagnostic ions are 91, 145, 177, 205 and 220; ii) for BP peak (start time: 8.80 min, ion dwell time: 30 ms) the $m/z$ ratios recorded are 51, 77, 105, 152 and 182; and iii) for DiBP and DiBP-d$_4$ peaks (start time: 9.80 min, ion dwell time: 10 ms), the diagnostic ions for DiBP are 104, 150, 167, 205 and 223, whereas the $m/z$ ratios selected for DiBP-d$_4$ are 80, 153, 171, 209 and 227.

### 2.7. Software

Scan control and data acquisition are performed using a MSD ChemStation version E.02.01.1177 (Agilent Technologies, Inc.) with Data Analysis software. PLS_Toolbox 8.5.2 (Wise et al., 2018) software for use within the MATLAB environment (version 9.3.0.713579, R2017b) MATLAB (2017) is used to perform the PARAFAC decomposition. STATGRAPHICS Centurion XVIII (version 18.1.11, 2018) is used to fit and validate the regression models.

## 3. Results and discussion

Tolerance intervals for the unequivocal identification of the analytes are established at the beginning of the study. Then, the presence of the additives in coffee, released from coffee capsules, and in Milli-Q water is studied.

### 3.1. Tolerance intervals for unequivocal identification of analytes

The requirements for the unequivocal identification of the analytes which are followed in this work appear in the analysis of food contact materials laid down in EUR 24105 EN, but using 3 $m/z$ ratios as is stated in 2002/657/EC Commission Decision, which is a stricter regulation about the unequivocal identification of compounds.

The fourteen reference standards are analysed to establish the permitted tolerance intervals.The clean-up of the TDU-PTV-GC–MS system is controlled throughout the analysis by the injection of six system blanks (TDU liners with no stir bar), one at the beginning of the chromatographic sequence, four among the most concentrated reference standards, and the last one at the end. So, a total of 20 injections are conducted in this first experiment.

The chromatographic peaks of DiBP and DiBP-d$_4$ overlap strongly because the structures of both analytes are very similar; for that reason, PARAFAC decomposition is used due to its capability to detect and handle overlapping and the effect of any unexpected or unknown interferent which could be present in complex matrix samples (Ortiz et al., 2020), such as coffee.

The abundance data for all the analytes are extracted from the chromatograms obtained after baseline correction. Then, a three-way array $\underline{X}$ (of dimension $I \times J \times K$) containing the data matrices of system blanks and reference samples is built for each analyte, except for DiBP and DiBP-d$_4$ that are analysed from a single array. The first dimension of each three-way array refers to the chromatographic way (the $I$ elution times), the second one to the spectral way (the abundances measured at $J$ $m/z$ ratios for each acquisition window), and the third one to the sample way (the $K$ samples). Table 1 shows the dimensions of the three-way arrays together with some features of the model estimated in each case by the PARAFAC decomposition.

The trilinearity of the experimental three-way arrays, when the number of factors is greater than or equal to two, is measured by the core consistency diagnostic index (CORCONDIA) (Bro & Kiers, 2003). Two factor models are estimated from the three-way array of BHT and that of DiBP window (that is, of DiBP and IS). The CORCONDIA index is greater than 98 % for these models. So, trilinearity of the data is guaranteed and therefore the unequivocal identification of the target analytes and the IS.

Fig. 1 shows the loadings of the PARAFAC decomposition from DiBP window. The chromatographic profile of the two factors, Fig. 1a, shows that the chromatographic peaks of both DiBP (purple solid line) and

**Table 1**

Characteristics of the PARAFAC models obtained from the decomposition of each data array built for every analyte.

| | BHT | BP | DiBP and DiBP-$d_4$ |
|---|---|---|---|
| **Tolerance intervals** | | | |
| Dimension[a] | $(53 \times 5 \times 20)$ | $(41 \times 5 \times 20)$ | $(67 \times 10 \times 20)$ |
| Number of factors | 2 | 1 | 2 |
| Non-negativity constraints | In the three modes | None | In the three modes |
| Explained variance (%) | 99.9 | 99.6 | 99.3 |
| CORCONDIA (%)[b] | 98 | – | 100 |
| **Coffee and Milli-Q water analysis** | | | |
| **Day 1** | | | |
| Dimension[a] | $(53 \times 5 \times 25)$ | $(41 \times 5 \times 25)$ | $(67 \times 10 \times 25)$ |
| Number of factors | 3 | 1 | 2 |
| Non-negativity constraints | In the three modes | None | In modes 1 and 2 |
| Explained variance (%) | 99.5 | 99.5 | 98.5 |
| CORCONDIA (%)[b] | 100 | – | 100 |
| **Day 2** | | | |
| Dimension[a] | $(53 \times 5 \times 25)$ | $(41 \times 5 \times 25)$ | $(67 \times 10 \times 25)$ |
| Number of factors | 3 | 1 | 2 |
| Non-negativity constraints | In the three modes | None | In modes 1 and 2 |
| Explained variance (%) | 99.5 | 99.0 | 98.3 |
| CORCONDIA (%)[b] | 100 | – | 100 |

[a] The dimension (scans $\times$ ions $\times$ samples) of the three-way arrays.
[b] The CORCONDIA index cannot be calculated in the PARAFAC decomposition with only one factor.

DiBP-$d_4$ (orange dashed line) are strongly overlapped as obviously expected. In addition, despite choosing different $m/z$ ratios to identify each compound, both analytes share most of the $m/z$ ratios recorded, as Fig. 1b shows, including the base peaks of both compounds ($m/z = 150$ and $m/z = 153$), which means that all the relative ion abundances of the diagnostic ions would be wrongly calculated in the case that the corresponding spectra are not successfully extracted. PARAFAC decomposition makes it possible to find the contribution to both profiles of each factor, and therefore of each compound.

Fig. 1c shows the increasing order of the DiBP loadings (purple circles) with the growing concentration of the eleven reference standards (2–9, 11, 13 and 15) and the constant values, corresponding to a certain concentration level, for samples 17–19, where only the concentration of IS (DiBP-$d_4$) varies. However, the loadings for DiBP-$d_4$ (orange dashed circles) are essentially the same for the eleven reference standards with a fixed IS concentration, whereas the higher the IS concentration the higher the loading for samples $17-19$. The latter samples are included in the data array to provide the PARAFAC method with enough information to the characteristic profiles of the IS, versus those of DiBP. The six system blanks (1, 10, 12, 14, 16 and 20) have null values for the loadings of both factors, as expected since no analyte is injected.

Fig. 2 shows the profiles of the PARAFAC decomposition estimated from BHT data array. An interferent, which gives rise to the second factor (green dashed line), is overlapped with BHT (blue solid line) in the chromatographic profile (Fig. 2a), although the size of the interferent peak is quite small in relation to that of BHT (see zoom in Fig. 2a). In addition, the spectral profiles in Fig. 2b show that the interferent (green dashed bars) shares the $m/z$ ratios 91, 145 and 177 with BHT (blue solid bars). For these reasons, it is important to find and distinguish the profiles of both analytes, BHT (analyte of interest) and the interferent.

Fig. 2c shows the sample profiles. As in the previous case, loadings for system blanks samples (1, 10, 12, 14, 16 and 20) are null for the two factors, as expected. The loadings for the factor related to BHT (blue solid circles) show the expected pattern, analogous to that of DiBP in Fig. 1c for the reference samples (2–9, 11, 13 and 15); the higher the
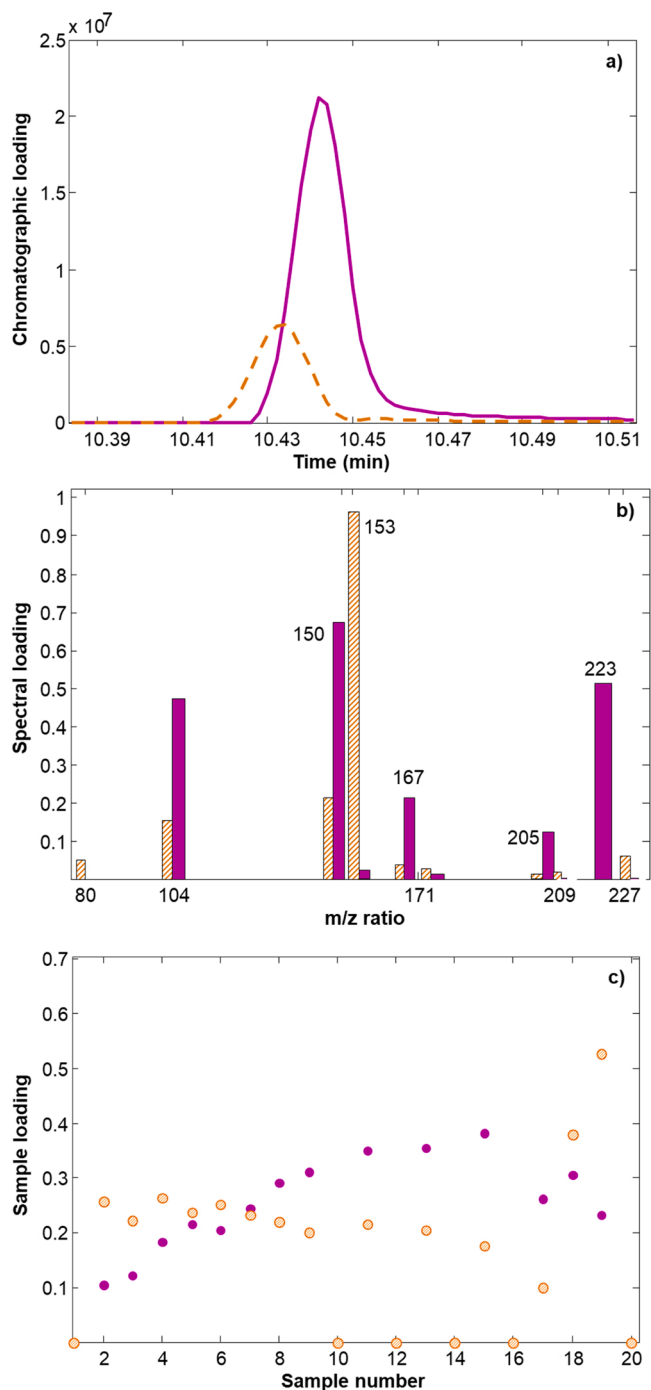
**Fig. 1.** Loadings for a) chromatographic, b) spectral, and c) sample profiles of the two factor PARAFAC model estimated from the reference standards for DiBP and DiBP-$d_4$. Factor 1 (DiBP) is in solid purple and factor 2 (DiBP-$d_4$) is in dashed orange. Sample numbers correspond to system blanks (1, 10, 12, 14, 16, and 20) and reference samples with increasing concentration of DiBP and constant concentration of DiBP-$d_4$ (2-9, 11, 13 and 15) or with constant concentration of DiBP and increasing concentration of DiBP-$d_4$ (17-19).

concentration the larger the loading. The loadings for the interferent (green dashed circles) are almost constant from sample to sample, compared to the values loadings for factor 1 (blue circles) that increased with BHT concentration.

Table 2 shows the tolerance intervals for both relative time and relative ion abundances estimated from the chromatographic and spectral profiles of the above PARAFAC decompositions.

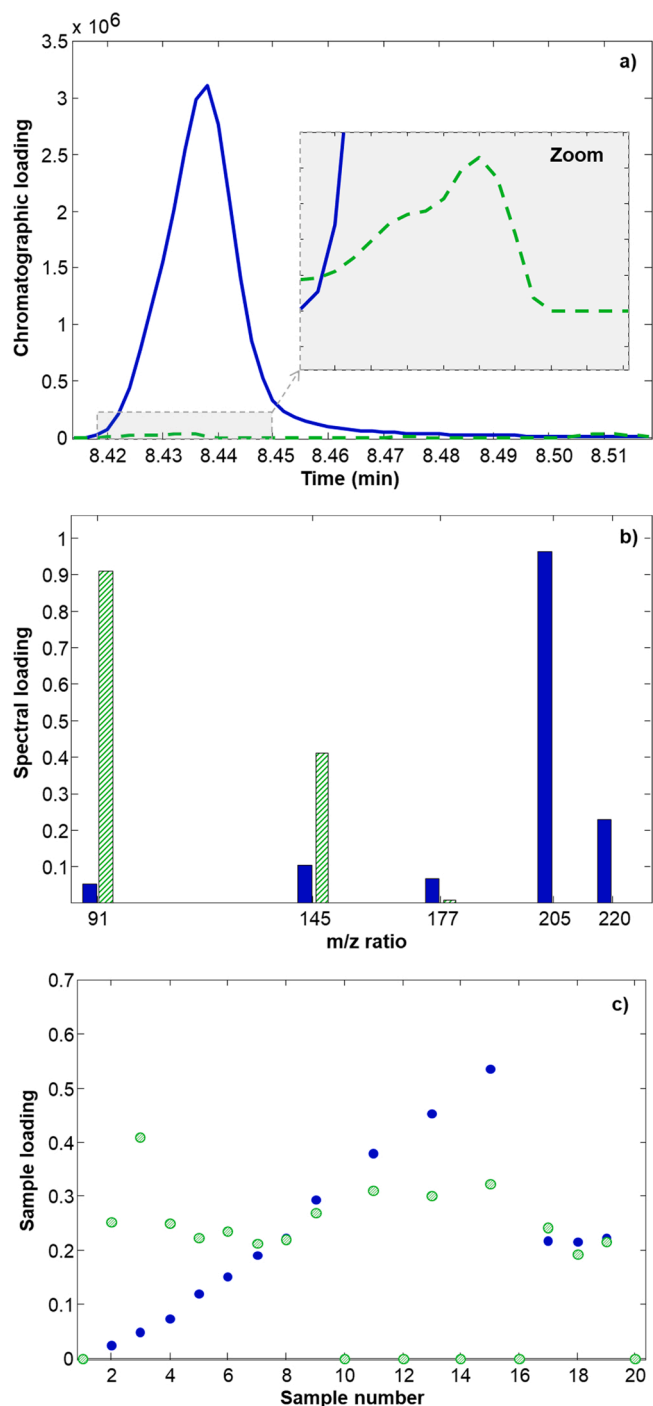The tolerance intervals for the relative retention time (the ratio of the

**Fig. 2.** Loadings for a) chromatographic, b) spectral, and c) sample profiles of the two factor PARAFAC model estimated from the reference standards for BHT. An enlarged view of the loadings of an interferent is shown in subplot a. Factor 1 (BHT) is in solid blue, factor 2 (an interferent) is in dashed green. Sample numbers correspond to system blanks (1, 10, 12, 14, 16, and 20) and reference samples with increasing concentration of BHT and constant concentration of IS (2-9, 11, 13 and 15) or with constant concentration of BHT and increasing concentration of IS (17-19).

chromatographic retention time of the analyte to that of the internal standard) are estimated with a margin of ±0.5 % according to EUR 24105EN (2009).

The tolerance intervals for the relative ion abundances are built according to EUR 24105 EN. The tolerance margin is ±50 % for relative intensities lower or equal to 10 %; ±20 % for relative intensities from 10

**Table 2**

Tolerance intervals built from reference samples for the relative retention time, and for the relative ion abundances to diagnostic ions and their application to the unequivocal identification of the analytes in Milli-Q water and coffee samples.

| Retention time | | | | | |
|---|---|---|---|---|---|
| Analyte | $t_R$ (min) | Relative $t_R$ | Tolerance interval | Relative retention time | |
| | | | | Day 1 | Day 2 |
| BHT | 8.44 | 0.810 | (0.806−0.814) | 0.810 | 0.810 |
| BP | 9.21 | 0.883 | (0.879−0.888) | 0.884 | 0.883 |
| DiBP-$d_4$ | 10.4 | 1.00 | (0.995−1.01) | 1.00 | 1.00 |
| DiBP | 10.4 | 1.00 | (0.996−1.01) | 1.00 | 1.00 |

| Relative ion abundances | | | | | | |
|---|---|---|---|---|---|---|
| Analyte | m/z ratio | Spectral loading | Relative abundance (%) | Tolerance interval (%) | Relative abundance (%) | |
| | | | | | Day 1 | Day 2 |
| BHT | 91 | 0.052 | 5.41 | (2.71−8.12) | 5.79 | 5.61 |
| | 145 | 0.102 | 10.6 | (8.46−12.7) | 10.6 | 10.5 |
| | 177 | 0.065 | 6.78 | (3.39−10.2) | 6.95 | 6.81 |
| | 205[a] | 0.964 | 100 | – | 100 | 100 |
| | 220 | 0.230 | 23.9 | (20.3−27.5) | 24.2 | 24.2 |
| BP | 51 | 0.138 | 18.2 | (14.6−21.8) | 17.4 | 17.9 |
| | 77 | 0.424 | 55.9 | (50.3−61.5) | 53.9 | 54.3 |
| | 105[a] | 0.759 | 100 | – | 100 | 100 |
| | 152 | 0.034 | 4.52 | (2.26−6.78) | 4.60 | 4.59 |
| | 182 | 0.474 | 62.5 | (56.2−68.7) | 64.7 | 65.0 |
| DiBP-$d_4$ | 80 | 0.0477 | 4.96 | (2.48−7.44) | 4.84 | 5.11 |
| | 153[a] | 0.961 | 100 | – | 100 | 100 |
| | 171 | 0.027 | 2.85 | (1.43−4.28) | 3.60 | 3.70 |
| | 209 | 0.016 | 1.66 | (0.83−2.50) | 1.68 | 1.83 |
| | 227 | 0.060 | 6.26 | (3.13−9.40) | 6.62 | 6.58 |
| DiBP | 104 | 0.474 | 70.5 | (63.5−77.6) | 68.2 | 68.1 |
| | 150[a] | 0.672 | 100 | – | 100 | 100 |
| | 167 | 0.212 | 31.6 | (26.9−36.4) | 33.8 | 33.3 |
| | 205 | 0.124 | 18.4 | (14.7−22.1) | 19.2 | 19.2 |
| | 223 | 0.514 | 76.2 | (68.8−84.1) | 77.1 | 77.8 |

[a] Base peak.

% to 20 %; ±15 % for relative intensities from 20 % to 50 %; and ±10 % for relative intensities higher than 50 %. PARAFAC decomposition provides a unique spectral profile for each analyte that is common to all the samples of the three-way array. So, for each *m/z* ratio a spectral loading is obtained in this decomposition, which is used to calculate the relative ion abundances: the ratio of the spectral loading to that of the base peak. Details of the procedure for establishing the tolerance intervals can be seen in Arroyo, Ortiz, Sarabia, and Palacios (2008) and Ortiz et al. (2020).

### 3.2. Spiked coffee and Milli-Q water samples

An initial study shows that Milli-Q water contains different amounts of the target analytes. Fig. 3 shows the additive residue concentration found in Milli-Q water (where IS is added) supplied by the water purification system on eight different days. The values vary considerably from day to day. As can be seen in Figs. 3b and 3c, a similar pattern is followed by BP and DiBP concentrations, which are decreasing during the first four days, and then both concentrations follow the same irregular pattern. This could mean that both analytes come from the same source and follow a similar releasing rate. On the other hand, the pattern followed by the concentration of BHT, Fig. 3a, is different from that of the other two analytes.

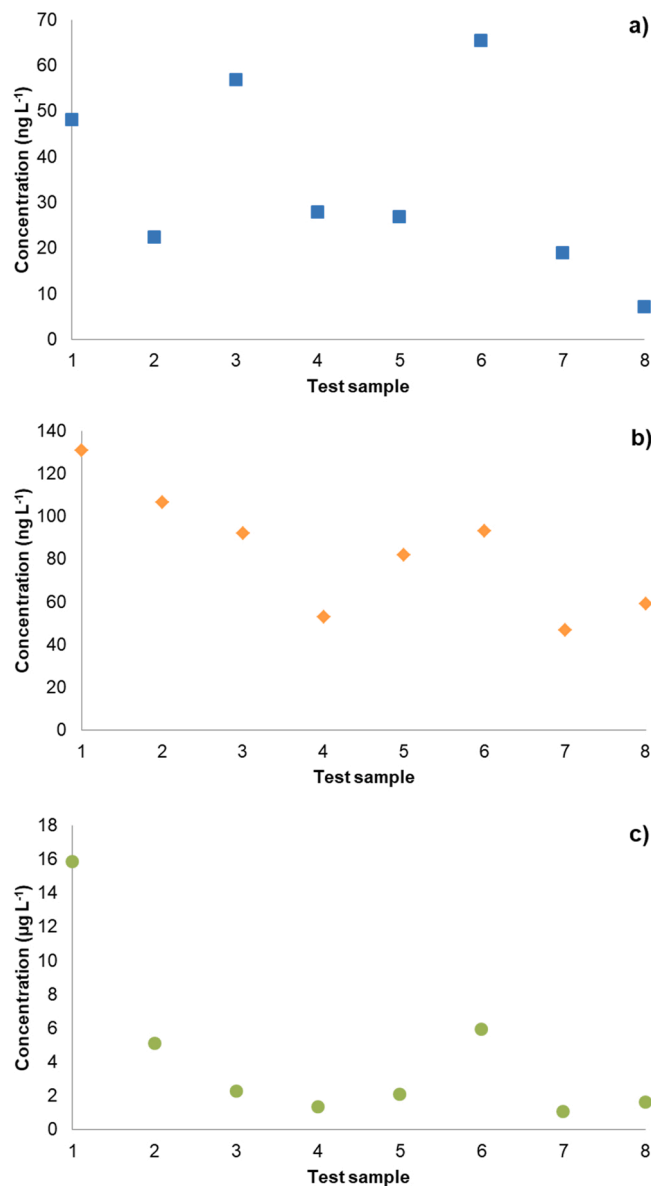Table 3 shows the average concentration, standard deviation and the

**Fig. 3.** Predicted concentration for each analyte in the Milli-Q water in different days: a) BHT, b) BP and c) DiBP.

coffee samples.

Thus, an experimental strategy, based on standard addition coupled to PARAFAC, is planned to quantify the concentration of the plastic additives both in the Milli-Q water and in the coffee samples. Fig. 4 shows total ion chromatograms (TIC) obtained both from Milli-Q and coffee samples, unfortified and fortified with intermediate concentrations of the analytes. More numerous chromatographic peaks are recorded in the coffee samples so, in addition to the overlapping of the peaks of DiBP and DiBP-$d_4$ shown in Section 3.1, unknown co-eluents could interfere in the determination of the target compounds. One way to address this issue is based on using the PARAFAC decomposition, which is a powerful tool in chromatography in order to model the underlying contribution of target compounds (Ortiz et al., 2020). On the other hand, preliminary studies highlighted the existence of matrix effect when coffee is analysed, so the standard addition method is used in order to obtain reliable results.

Two different fortification levels for the target plastic additives in coffee are studied. Each fortification level is approached in a separate analysis session, so an entire study is performed in two different days: day 1 and day 2.

A total of 25 chromatographic runs are conducted in each analysis session: 6 coffee samples fortified with the target additives and a fixed IS content (runs 2–7), 2 coffee samples fortified with the IS and fixed amounts of the target additives (runs 8 and 9), 6 Milli-Q water samples fortified with the target additives and a fixed IS content (runs 12–17), 2 Milli-Q water samples fortified with the IS and fixed amounts of the target additives (runs 18 and 19), 4 Milli-Q water samples with a fixed IS content (runs 20–23), and finally 5 system blanks for testing the clean-up of the GC–MS system (runs 1, 10, 11, 24 and 25).

Abundance data are arranged in three-way arrays, as previously, and PARAFAC models are then built for the compounds; the characteristics of these models are shown in Table 1. The CORCONDIA index is 100 % in all cases. As in Section 3.1, models with 1 and 2 factors are built for BP and DiBP- DiBP-$d_4$, respectively. However, the models for BHT require one factor more than that in Section 3.1; in fact, a 3 factor model is needed for modelling the two interferents that coelute with the BHT peak when coffee samples are included in the three-way array. In all cases, the target compounds are unequivocally identified considering the tolerance intervals in Table 2, since the retention times and relative ion abundances of the corresponding PARAFAC profiles are inside these intervals.

On the other hand, Fig. 5 shows the sample loadings of the PARAFAC decomposition obtained for BHT from the data of day 1. Samples of coffee (samples 2–7) and Milli-Q water (samples 12–17) are fortified with equal spiked concentration of BHT, but the sample loadings are significantly lower for the coffee samples (Fig. 5b shows in detail the coffee samples pattern). The same occurs for coffee samples 5, 8 and 9, and Milli-Q water samples 15, 18 and 19, which are fortified with the same level of BHT and have similar sample loadings in each case, but lower loadings are found for coffee samples again. All of this confirms the existence of a strong matrix effect, which may occur in SBSE and/or GC–MS steps. The matrix effect makes it necessary to apply the standard addition method for quantification of the target analytes.

Table 4 shows the parameters of the standard addition models fit for each target analyte taking as dependent variable the sample loading and as independent variable the spiked concentration of the analyte. Outliers, data with studentized residuals in absolute value greater than 3, are removed in each case.
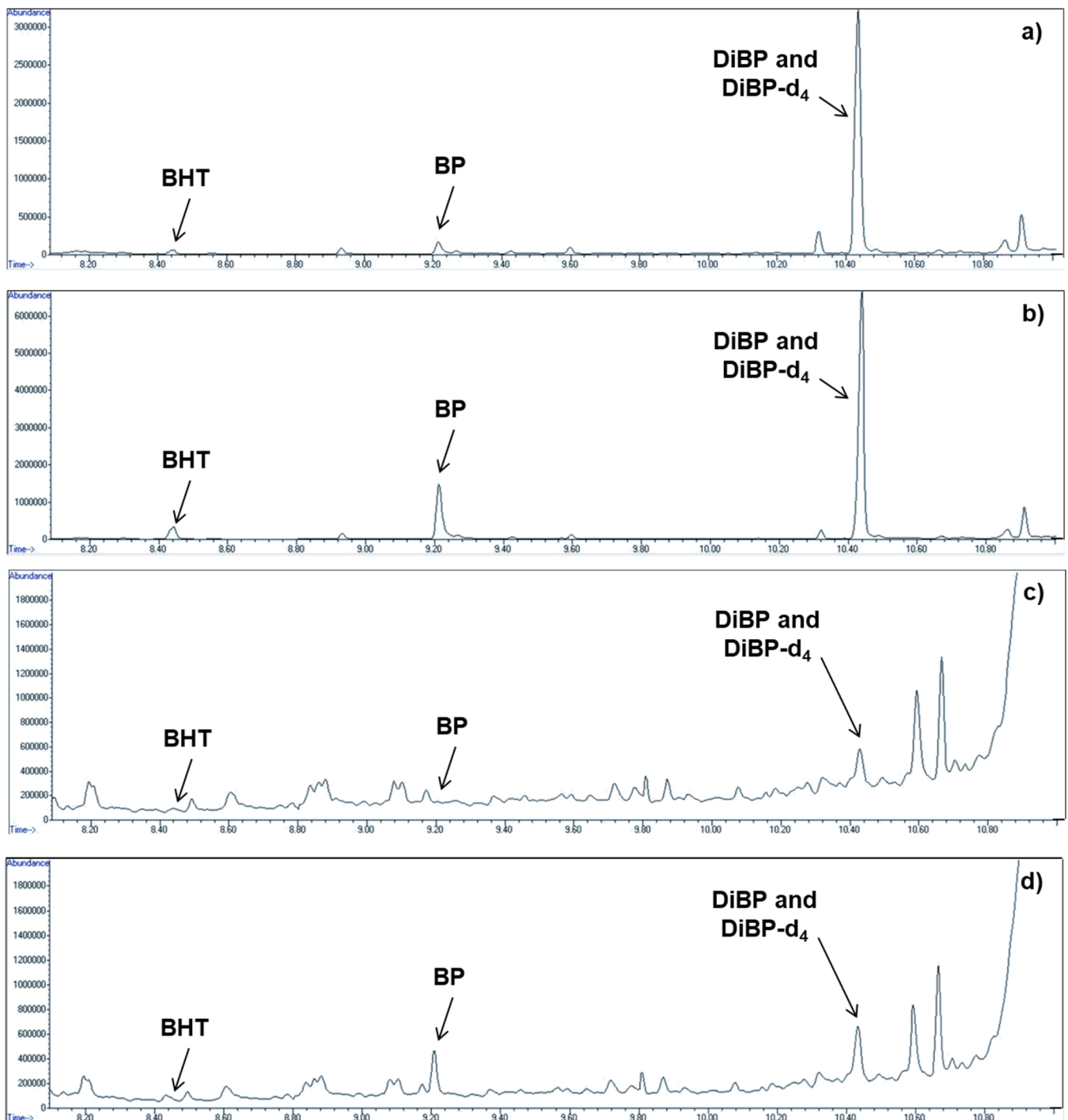
lowest and highest values of BHT, BP and DiBP concentration found on eight different days for Milli-Q water samples. Higher amounts of DiBP (4.42 µg $L^{-1}$ on average) are found with respect to that of BHT and BP (34.3 and 83.0 ng $L^{-1}$ on average, respectively); whereas more dispersion may be noted for DiBP, with standard deviation nearly 4.96 µg $L^{-1}$, than for BHT and BP, whose standard deviations are in the order of 25 ng $L^{-1}$. Concentration variations may be highly dependent on the period of time in which water remains within the purification system plastic tank or on the tank's water level. So, the water has to be drawn from the tank at once just before used for each analysis session. In addition, the levels of the plastic additive in the water have to be determined in order to avoid possible errors when quantifying the additives in the brewed

**Table 3**

Statistics for the additive residues concentrations found in Milli-Q water with IS on eight different days.

| Test number | Analytes | Average | Standard deviation | Minimum | Maximum | Range |
|---|---|---|---|---|---|---|
| 8 | BHT (ng $L^{-1}$) | 34.3 | 20.3 | 7.29 | 65.5 | 58.2 |
| 8 | BP (ng $L^{-1}$) | 83.0 | 28.8 | 46.9 | 131 | 83.9 |
| 8 | DiBP (µg $L^{-1}$) | 4.42 | 4.96 | 1.05 | 15.9 | 14.8 |

**Fig. 4.** Total ion chromatograms of day 2 obtained from the injection of: a) Milli-Q water with IS at 250 ng L$^{-1}$; b) Milli-Q water spiked with BHT and BP at 500 ng L$^{-1}$, DiBP at 2000 ng L$^{-1}$ and IS at 250 ng L$^{-1}$; c) coffee with IS at 1000 ng L$^{-1}$; d) coffee spiked with BHT at 1000 ng L$^{-1}$, BP and DiBP at 6000 ng L$^{-1}$ and IS at 1000 ng L$^{-1}$.

If PARAFAC models are built from three-way arrays formed by only the spiked Milli-Q water samples, and the regression models "sample loading" vs. "spiked concentration" are fitted, the performance of the procedure does not change significantly. Table 5 shows the characteristics of the regression models fitted in this case, which are very similar to that in Table 4. This confirms that PARAFAC decomposition models successfully the contribution of the target analytes to the acquired signals, even in the presence of other complex matrix components.

The concentrations found for both Milli-Q water and coffee samples are shown in Table 4. The Milli-Q water samples present differences in concentration depending on the day, as already seen in Fig. 3 and Table 3. The final values estimated for the coffee samples are the result of subtracting the concentrations found in the Milli-Q water the corresponding day. The lowest concentration of additive in Milli-Q water samples corresponds to BHT (18.30 and 8.30 ng L$^{-1}$ for days 1 and 2, respectively). The amounts of the additive residues found in Milli-Q water samples, which are released from the laboratory materials and systems, can be high for ultra-trace analysis and should be subtracted from the results of coffee. For example, if the 18 ng L$^{-1}$ found for BHT in Milli-Q water are not considered, it would result in an error of around
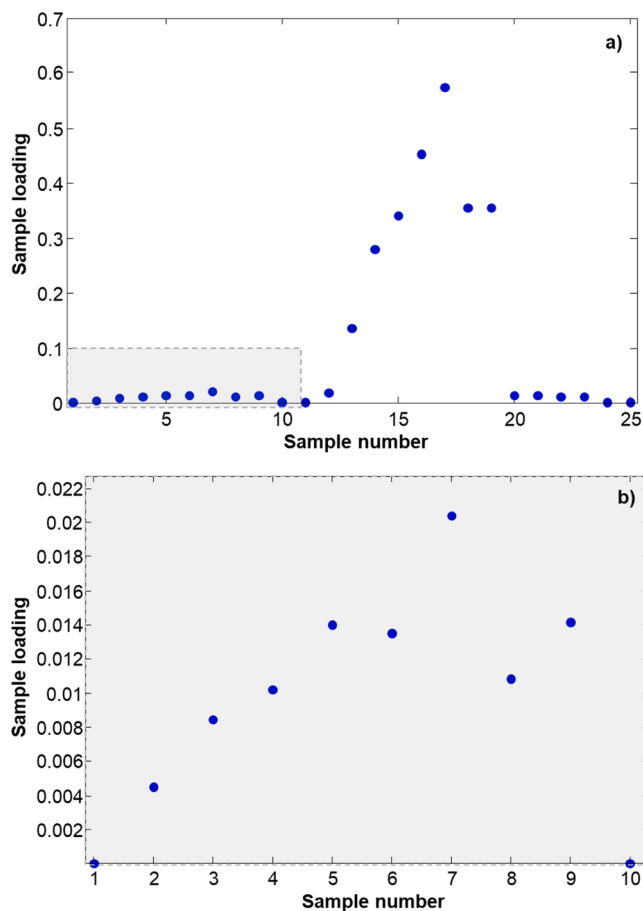
**Fig. 5.** (a) Sample loadings for the factor of the PARAFAC model (day 1) related to BHT, and (b) enlarged view. Samples: coffee samples fortified with the target analytes and a fixed IS amount (2-7), coffee samples fortified with IS and fixed amounts of the target analytes (8-9), Milli-Q water samples fortified with the target analytes and a fixed IS content (12-17), Milli-Q water samples fortified with the IS and fixed amounts of the target analytes (18-19), Milli-Q water samples with a fixed IS content (20-23), system blanks (runs 1, 10, 11, 24 and 25).

5%, when determining the amount of BHT in coffee, nearly 360 ng L$^{-1}$. However, for BP and DiBP, the errors could be as much as 40 % if the residues of these additives in the water are not considered.

For this reason, the values found in the Milli-Q water are subtracted from the concentrations in coffee samples calculated for each day. The concentrations found in coffee samples are 341 and 333 ng L$^{-1}$ of BHT; 132 and 72.3 ng L$^{-1}$ of BP; and 1.67 and 1.32 µg L$^{-1}$ of DiBP, for days 1 and 2, respectively. The concentration released from the coffee capsules into solid coffee are 2.84 and 2.77 µg kg$^{-1}$ of BHT; 1.10 and 0.602 µg kg$^{-1}$ of BP; and 13.9 and 11.0 µg kg$^{-1}$ of DiBP, for days 1 and 2, respectively. Given the uncertainty concerning the values found for DiBP, no statistically significant conclusions may be obtained and, as a consequence, there is no statistical evidence that these values are above the specific migration limit. The concentrations of all the additives released from the coffee capsules comply with the regulation since the values found are below, or around, in the case of DiBP, the specific migration limits established by Commission Regulation (EU) 10/2011.

## 4. Conclusions

The concentration of BHT, BP and DiBP found in Milli-Q water depends on the day of collection of water. For this reason, the analysis of the coffee and Milli-Q water samples should be done on the same day. In this way, the traces of the additives found in the Milli-Q water samples

**Table 4**
Parameters of the calibration models and concentrations found, on two different days, in Milli-Q water and coffee samples.

| Day | Sample | Standard addition | Analyte | | |
|---|---|---|---|---|---|
| | | | BHT | BP | DiBP |
| Day 1 | Milli-Q water | Intercept | −3.61 10$^{-2}$ | 8.67 10$^{-2}$ | 3.82 10$^{-1}$ |
| | | Slope | 1.98 10$^{-3}$ | 1.85 10$^{-3}$ | 3.62 10$^{-4}$ |
| | | r* | 0.980 | 0.987 | 0.961 |
| | | s$_{yx}$ (ng L$^{-1}$)** | 2.11 10$^{-1}$ | 1.58 10$^{-1}$ | 2.19 10$^{-1}$ |
| | | Concentration (µg L$^{-1}$) | 0.018 | 0.047 | 1.053 |
| | Coffee | Intercept | 5.73 10$^{-1}$ | 1.05 10$^{-1}$ | 7.65 10$^{-1}$ |
| | | Slope | 1.60 10$^{-3}$ | 5.88 10$^{-4}$ | 2.81 10$^{-4}$ |
| | | r* | 0.957 | 0.951 | 0.995 |
| | | s$_{yx}$ (ng L$^{-1}$)** | 2.67 10$^{-1}$ | 1.00 10$^{-1}$ | 6.31 10$^{-2}$ |
| | | Concentration in brewed coffee (µg L$^{-1}$) | 0.341 | 0.132 | 1.674 |
| | | Concentration in solid coffee (µg kg$^{-1}$) | 2.84 | 1.10 | 13.9 |
| Day 2 | Milli-Q water | Intercept | 1.54 10$^{-2}$ | 1.02 10$^{-1}$ | 4.60 10$^{-1}$ |
| | | Slope | 1.86 10$^{-3}$ | 1.70 10$^{-3}$ | 2.81 10$^{-4}$ |
| | | r* | 0.987 | 0.999 | 0.999 |
| | | s$_{yx}$ (ng L$^{-1}$)** | 1.58 10$^{-1}$ | 3.25 10$^{-2}$ | 3.64 10$^{-2}$ |
| | | Concentration (µg L$^{-1}$) | 0.008 | 0.059 | 1.640 |
| | Coffee | Intercept | −2.78 10$^{-1}$ | 2.62 10$^{-2}$ | 1.84 10$^{-1}$ |
| | | Slope | 8.16 10$^{-4}$ | 1.99 10$^{-4}$ | 6.20 10$^{-5}$ |
| | | r* | 1.000 | 1.000 | 0.993 |
| | | s$_{yx}$ (ng L$^{-1}$)** | 2.07 10$^{-2}$ | 3.03 10$^{-2}$ | 4.62 10$^{-2}$ |
| | | Concentration in brewed coffee (µg L$^{-1}$) | 0.333 | 0.072 | 1.319 |
| | | Concentration in solid coffee (µg kg$^{-1}$) | 2.77 | 0.602 | 11.0 |

\* r: linear correlation coefficient.
\*\* s$_{yx}$: standard error of estimation.

**Table 5**
Parameters of the calibration models for the analyses performed with only Milli-Q water samples.

| Days | Spiked Milli-Q water samples | Analytes | | |
|---|---|---|---|---|
| | | BHT | BP | DiBP |
| 1 | Calibration model | y = -3.76 10$^{-2}$ + 1.98 10$^{-3}$ x | y = 8.67 10$^{-2}$ + 1.85 10$^{-3}$ x | y = 3.82 10$^{-1}$ + 3.63 10$^{-4}$ x |
| | r* | 0.980 | 0.987 | 0.961 |
| | s$_{yx}$ (ng L$^{-1}$)* | 2.11 10$^{-1}$ | 1.57 10$^{-1}$ | 2.19 10$^{-1}$ |
| 2 | Calibration model | y = 1.35 10$^{-2}$ + 1.85 10$^{-3}$ x | y = 1.02 10$^{-1}$ + 1.72 10$^{-3}$ x | y = 4.59 10$^{-1}$ + 2.79 10$^{-4}$ x |
| | r* | 0.987 | 0.999 | 0.999 |
| | s$_{yx}$ (ng L$^{-1}$)* | 1.58 10$^{-1}$ | 3.34 10$^{-2}$ | 3.60 10$^{-2}$ |

\* r: linear correlation coefficient; s$_{yx}$: standard error of estimation.

may be subtracted.

The standard addition method is required to obtain the actual concentration of each analyte, which is migrated from coffee capsules, because of the matrix effect.

The SBSE technique is suitable for extracting and concentrating the low concentration of the analytes in Milli-Q water and coffee samples.

PARAFAC decomposition enables the unequivocal identification and quantification of each analyte according to the requirements established by EU regulations currently despite that some target analytes share $m/z$

ratios with coeluting interferents. In fact, successful results are achieved despite of the presence of complex matrix samples in the three-way array.

Traces of BHT, BP and DiBP released from the coffee capsules are found in coffee, with concentrations below, or around, in the case of DiBP, the specific migration limits established by Commission Regulation (EU) 10/2011.

## CRediT authorship contribution statement

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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