Supramolecular solvent-based microextraction of emerging bisphenol A replacements (colour developers) in indoor dust from public environments

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ABSTRACT

Bisphenol A (BPA) is present in a wide variety of materials and it is a well-known endocrine disruptor that is widespread in indoor and outdoor environments. For this reason, industry has introduced a variety of replacements, such as Bisphenol S (BPS) or Bisphenol F (BPF), and other less known structural analogs, such as BPS-MAE, D-8 or TGSA. These emerging potential contaminants have been identified in thermal paper products, according to recent studies, but their potential toxic effects and their migration into the environment remain unclear. In this study, we report for the first time the presence of emerging BPA replacements in indoor dust from public environments (shops, restaurants, etc.). For this purpose, we optimized a novel supramolecular solvent (SUPRAS)-based microextraction method. SUPRAS are multi-target solvents made up of self-assembled amphiphiles. They offer multiple extraction interactions (dispersion, polar, hydrophobic, etc.) and they constitute excellent candidates to develop generic and fast sample treatment procedures at low cost. By this method, emerging BPA replacements (BPS-MAE, D-8 and TGSA) were detected in dust at median concentrations in the range 6 – 22 $ng \cdot g^{-1}$ (around ten times lower than BPS) with detection frequencies in the range 50 – 90%. These results constitute a first insight into the migration of emerging BPA replacements into the environment via indoor dust, which is a common route of human exposure to contaminants.

Keywords: supramolecular solvents, indoor dust, bisphenol A, bisphenol S, BPS-MAE, D-8, TGSA

1. Introduction

Bisphenol A (BPA) or 4,4'-(propane-2,2-diyl)diphenol, is used worldwide and its production volume is one of the highest in the industry. It is used in wide variety of applications from food-related plastics (food-packaging, bottles, cookware, tableware, etc.) to other materials, such as medical devices, printing inks, thermal paper, etc. BPA can migrate into the environment because plastic contains non-polymerized monomer residues or because it is released by ester bonds hydrolysis under heat or reaction with the acid or basic contents of the bottles (Björnsdotter et al., 2017a). BPA has become an ubiquitous environmental contaminant, which is present in river waters (1.0 – 628 $ng \cdot L^{-1}$) (Suzuki et al.,2004; Ballesteros-Gómez et al., 2007; Ruiz et al., 2007; Yamazaki et al., 2015), sediments (3.94 – $2.2 \cdot 10^6$ $ng \cdot g^{-1}$ d.w.) (Terasaki et al., 2007; Liao et al., 2012a; Wang et al., 2016), sewage sludge (0.42 – 25,600 $ng \cdot g^{-1}$) (Song et al., 2014; Lee et al., 2015; Yu et al., 2015), air (indoor: <0.1 – 1.8 $ng \cdot m^{-3}$, outdoor: <0.1 – 2.5 $ng \cdot m^{-3}$) (Wilson et al., 2001) and dust (535 – 9,730 $ng \cdot g^{-1}$) (Geens et al., 2009). It has also been widely detected in biological samples, such as blood (0.79 – 7.12 $ng \cdot mL^{-1}$) (Owczarek et al., 2018) saliva (mean of 3.64 $\mu g \cdot L^{-1}$) (Lee et al., 2017) or urine (mean of 2.6 $\mu g \cdot L^{-1}$) (Casas et al., 2013). BPA is a well-known endocrine disruptor (Rochester, 2011), it is capable to disrupt the thyroid hormone action, affecting vertebrate development (Zhang et al., 2017) and it can act as neurodevelopmental toxicant too (Kincha et al., 2015).

In order to evade regulatory oversight and social pressure, industry has introduced BPA replacements into the market. Replacements are usually structural analogs to BPA with similar physicochemical properties and, subsequently, similar potential toxicity (Gramec Skledar and Peterlin Masic, 2016; Russo et al., 2018). Bisphenol S (BPS), bisphenol F (BPF), bisphenol B (BPB), bisphenol AF (BPAF), bisphenol E (BPE), tetrabromobisphenol A (TBBPA), bisphenol A diglycidyl ether

(BADGE) and bisphenol F diglycidyl ether (BFDGE) are common BPA replacements. They are used in a variety of materials too, such as electronic equipment, cans' lacquer coating, dental sealants and flame retarded products (Björnsdotter et al., 2017a). Due to this massive utilization, they have also been widely reported in sediments (3.2 – 12.6 $ng \cdot g^{-1}$), sewage sludge (12.8 – 4,730 $ng \cdot g^{-1}$) or indoor dust (0.15 – 4.18 $\mu g \cdot g^{-1}$), etc. (sum of all detectable analogues including BPA) (Chen et al., 2016).

Other widespread use of BPA is thermal paper (Geens et al., 2012; ,Björnsdotter et al., 2017a; Pivnenko, 2018). Replacements have also been introduced into the market for this aim, namely BPS and other less known compounds such as 4-hydroxyphenyl 4-isopropoxyphenyl Sulfone (D-8), 4,4′-sulfonylbis(2-allylphenol) (TGSA), 4-((4-(allyloxy)phenyl)sulfonyl)phenol (BPS-MAE), Pergafast 201 and D-90 (US EPA, 2015). Although there are some recent studies about the presence of these compounds in thermal paper products and their potential toxic effects (Goldinger et al. 2015; Björnsdotter et al., 2017b; Eckardt and Simat, 2017) their migration and presence in the environment have not been assessed so far.

Indoor dust is a potential source of human exposure to BPA and its analogs due to their migration from many materials and slow degradation (Rudel et al., 2003; Völkel et al., 2008; Geens et al., 2011 and 2012). Concentration values in indoor dust usually range from $ng \cdot g^{-1}$ to $\mu g \cdot g^{-1}$ levels. Levels up to 39,000 $ng \cdot g^{-1}$ of BPA and up to 26,600 of BPS $ng \cdot g^{-1}$ have been reported in different countries from US and Asia (Liao et al. 2012b; Wang et al. 2015). In the present study, BPA replacements used in thermal paper (BPF, BPS, BPS-MAE, D-8, TGSA) (Table 1) were analyzed in indoor dust for the first time.

To carry out the study, a novel simultaneous extraction/clean-up method based on the use of supramolecular solvents (SUPRASs) was optimized. SUPRASs are nanostructured liquids produced from self-assembled amphiphilic compounds (Caballo et al., 2017; Ballesteros-Gómez et al., 2018). They are excellent extraction materials that offer multiple binding interactions (ionic, anionic, hydrogen bonds, dispersion interactions, etc.). Binding interactions can be adjusted for each purpose by switching the functional groups of the amphiphile and the nature of the coacervation-inducing agent (Caballo et al., 2017; Ballesteros-Gómez et al., 2018). Their nanostructure give rise to microenvironments of different polarity and confer them restricted access properties for the exclusion of macromolecules, which are common interferents in analytical applications (Ballesteros-Gómez et al., 2012). Further advantages are their easy synthetic procedures, non-volatility and non-flammability (Caballo et al., 2017; Ballesteros-Gómez et al., 2018). All these properties make them excellent candidates for generic sample treatment of indoor dust, a complex and heterogeneous matrix containing from textile and paper fibers to human or animal hair, cells and mineral components, among others. Dust samples were collected in public environments, because of the frequent use of thermal paper cash receipts. Results constitute a first insight into the possible migration of these contaminants into the environment.

2. Materials and methods

2.1. Chemicals and reagents

All solvents were of analytical reagent-grade and were used as supplied. Methanol (MeOH) and tetrahydrofuran (THF) were acquired from VWR – Prolabo Chemicals (Bois, France). 1- Octanol and 1- Decanol, were obtained from Sigma-Aldrich (St. Louis, MO, USA), while 1- Hexanol was supplied by Merck (Darmstadt,

Germany). Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Madrid, Spain).

A standard reference material (SRM) Trace Metals - Baghouse Dust was used for optimization and validation purposes. It was purchased from Sigma-Aldrich (St. Louis, MO, USA).

The target compounds: 4,4'-(propane-2,2-diyl) diphenol (bisphenol A, BPA), 4,4'-Sulfonyldiphenol (bisphenol S, BPS) and 4,4'-Methylenediphenol (bisphenol F, BPF) were acquired from Sigma-Aldrich (St. Louis, MO, USA). 4-(4-propan-2-yloxyphenyl)sulfonylphenol (D-8), 4-(4-hydroxy-3-prop-2-enylphenyl)sulfonyl-2-prop-2-enylphenol (TGSA) and 4-(4-phenylmethoxyphenyl)sulfonylphenol (BPS-MAE) were obtained from Toronto Research Chemicals (Toronto, Canada). The internal standards (IS) Bisphenol A-d_6 diglycidyl Ether (BPA-d_6) and bis(4-hydroxyphenyl) Sulfone-d_8 (BPS-d_8) were also obtained from Toronto Research Chemicals.

Stock solutions of individual bisphenols (2 $mg \cdot mL^{-1}$) were prepared in MeOH and stored at -20ºC. A spike solution of internal standards (BPS-d_8 and BPA-d_6) was prepared in MeOH at a concentration of 5 $mg \cdot L^{-1}$ for optimization and for sample analysis. Intermediate and working solutions of bisphenols and of internal standards mixtures were prepared by appropriate dilution in MeOH and stored at -20ºC.

2.2. Apparatus

The analysis was carried out using an Agilent Technologies 1200 LC system with a column Phenomenex Luna® C_8 column (2.0 mm i.d., 100 mm length, 3.0 μm particle size) preceded by a precolumn Phenomenex KJ 0-4282 SecurityGuard Cartridge Kit, Ea. This was coupled to an Agilent Technologies 6420 Triple Quadrupole mass

spectrometer equipped with an electrospray ionization (ESI) source operating in negative mode. An additional LC column (Agilent Eclipse Plus C8 5 µm, 4.6 mm × 50 mm) was inserted between the pump and injector in order to trap possible bisphenols released from the instrument. Raw data was controlled and processed using Agilent MassHunter Software® (version B.07.00).

Other instrumentation used for sample preparation were a vortex-shaker REAX Top (Heidolph, Schwabach, Germany) and a 12 x 1.5 – 2 mL angle rotor Minicen centrifuge from Ortoalresa (Madrid, Spain).

2.3. SUPRAS method optimization

Optimization of SUPRAS was carried out by extraction of a mix dust (collected in two houses in Córdoba, sieved to 0.5 mm and homogenized), fortified at 5,000 $ng \cdot g^{-1}$ (BPA, BPF, BPS, D-8 and TGSA) and of internal standards (BPS-d_8 and BPA-d_6).

Dust aliquots (50 mg) were added to 2 mL Eppendorf microtubes, followed by SUPRAS synthetic solutions (120 – 200 µL of amphiphile and a mixture of water:THF up to 1.2 mL). Samples were vortex-stirred for 5 min for SUPRAS formation, sample dispersion and extraction, and centrifuged for 20 min at 10,000 rpm for phase separation. At the end, three phases were observed: SUPRAS (upper phase), equilibrium solution (in the middle, containing water:THF and a residual amount of amphiphile at the critical aggregation concentration) and the solid matrix (at the bottom). The SUPRAS phase, enriched with the target compounds, was diluted to 1 mL with MeOH to facilitate the optimization process by keeping constant the final volume and aliquots of 3 µL were directly injected into the LC-MS/MS system.

Both the final composition and microstructure characteristics of the SUPRAS depend on the nature and composition of the initial synthetic solution. A variety of SUPRAS were generated with different amphiphiles and by tuning the composition of the initial ternary mixture (amphiphile:water:THF) and tested for extraction. The following experimental conditions were studied: type of amphiphile (1-hexanol, 1-octanol and 1-decanol), concentration of amphiphile (10 – 16.67, % v/v) and concentration of THF (8.33 – 33.33, % v/v) for a final volume of 1.2 mL. Experiments were made in triplicate. Optimal conditions were selected on the basis of extraction efficiency and concentration factor [SUPRAS volume (µL)/ sample size (mg)].

2.4. SUPRAS method validation

The linearity, detection and quantitation limits and matrix effects of the method were assessed by running calibration with two dust samples, i.e. the in-house dust mix and the SRM Trace Metals - Baghouse Dust, and at two sample sizes (25 and 50 mg). Results were compared with those obtained from SUPRAS calibration. The optimal SUPRAS (synthetic conditions: 200 µL 1-hexanol, 200 µL THF, 800 µL water) was applied to dust samples fortified in the range 10 – 10,000 $ng \cdot g^{-1}$ of the target compounds and 5,000 $ng \cdot g^{-1}$ of IS mix (mix of BPA-d_6 and BPS-d_8 at 5 $mg \cdot L^{-1}$). Unfortified SUPRAS (blanks) and dust samples were also analysed (in triplicate). Levels of target compounds were below LODs in the blanks and in the two dust samples.

The limits of detection (LOD) and quantification (LOQ) ($ng \cdot g^{-1}$) of the method were estimated from a signal-to-noise ratio of 3 and 10, respectively.

2.5. Analysis of bisphenols

188 *2.5.1. Sample collection*

189 Sampling was performed using a vacuum cleaner with bags. Samples were
190 collected in Spain in 2018 from public environments (*n*=10): two electronic shops, two
191 clothing shops, one sport clothing shop, one decoration shop, three bazaars and one
192 cafeteria. Samples were homogenized and sieved to 0.5 mm.

193

194 *2.5.2. Hexanol - based SUPRAS extraction*

195 First, approximately an aliquot of 25 mg of dust was weighed in a 2 mL
196 Eppendorf microtube. The SUPRAS synthetic solution (200 µL of hexanol, 200 µL of
197 THF and 800 µL of water) was added and spiked with 25µL of IS mix. SUPRAS
198 formation and microextraction/clean-up was performed in a single-step by vortexing (5
199 min) and centrifugation at 10,000 rpm for 20 min. After phase-separation, 150 µL of
200 SUPRAS (the top layer) was collected, transferred to an LC vial and aliquots of 3 µL
201 measured by LC MS/MS. A schema is shown in Figure 1.

202

203 *2.5.3. Quantification of bisphenols by LC – MS/MS*

204 The mobile phase was made up of Milli-Q water (A) and MeOH (B) at a flow
205 rate of 0.25 $mL \cdot min^{-1}$. The injection volume was 3 µL. The gradient was as follow:
206 initial 100% A hold for 1 min and decreased to 30% in 5 min, holding for 7 min,
207 increased B to 100% and maintained for 6 min and finally re-conditioning for 7 min.

208 The MRM transitions for target masses are given in Table 2. BPA, BPF, BPS,
209 BPS-MAE, D-8 and TGSA were analyzed in ESI negative ionization mode.

The optimal source parameters were: gas temperature, 300 °C; gas flow, 11.0 $L \cdot min^{-1}$; nebulizer gas pressure, 15 psi; capillary voltage, -4500 V; MS1 heater, 100 °C; MS2 heater, 100 °C.

Quantitative analysis MassHunter workstation software from Agilent Technologies was used for quantification of bisphenols. Calibration was performed with SUPRAS in the range 10 – 10,000 $ng \cdot g^{-1}$ and by using the deuterated internal standard BPA-d_6, except for BPS, for which BPS-d_8 was used instead (at a final concentration of 5,000 $ng \cdot g^{-1}$).

3. Results and discussion

SUPRASs have been already successfully applied in the extraction of bisphenols from food (Ballesteros-Gómez et al., 2009), urine (García-Prieto et al. 2008; Salatti-Dorado et al., 2016), environmental waters and wastewaters (Ballesteros Gómez et al., 2007), etc.. SUPRASs are generated in a self-assembly and coacervation process that occurs on two scales (Caballo et al., 2017; Ballesteros-Gómez et al., 2018). First, amphiphiles form tridimensional aggregates (mainly micelles and/or vesicles) in solution. Then, aggregates self-assemble into a new highly packed phase (SUPRAS) by the stimuli of a coacervation-inducing agent (change of pH, temperature, addition of salt or addition of a poor solvent for the amphiphile). They are very tunable solvents whose composition and micro- or nano-structure change with the nature and composition of the synthetic solution (Ballesteros-Gómez et al., 2012; Ballesteros-Gómez et al., 2018).Both aspects influence recoveries of the target compounds and the simultaneous exclusion of interferents (usually macromolecules or polymers which are non-soluble in the SUPRAS medium or which are size-excluded due to the limited pore size of the SUPRAS network). In general, amphiphiles with longer alkyl chain length give rise to

more hydrophobic SUPRAS, which have less content in water and which also provide less energetic hydrogen bonds for extraction. Furthermore, SUPRAS with higher content in water produce bigger coacervate droplets and less packed structures. This usually results in better extraction efficiency for polar and moderate polar compounds, such as bisphenols (Salatti-Dorado et al., 2016; Ballesteros-Gómez et al., 2018). Phase diagrams (for SUPRAS formation) and composition of SUPRAS made up of inverse aggregates of 1-hexanol in THF:water have been recently reported by our group and they have been proven to be suitable for the extraction of BPA (Salatti-Dorado et al., 2016). For this reason they were selected for the study of novel BPA replacements. SUPRAS formation just requires mixing and centrifuging the synthetic solution for accelerating phase separation. Then, we observed two phases: the aqueous equilibrium solution at the bottom (containing the residual alcohol at a low critical micellar concentration) and the SUPRAS phase containing the majority of the amphiphile packed as an inverse hexagonal phase. Figure 2 shows a schema of the SUPRAS formation and its structure. The equilibrium solution helped to disperse the sample and favored the extraction process at such a low volume of SUPRAS phase (usually 100 – 500 µL). Furthermore, it acts as sink of polar interferents.

3.1. SUPRAS optimization

As preliminary experiments, SUPRAS blanks (without dust) were underwent extraction by changing the type of amphiphile (1-hexanol, 1-octanol and 1-decanol, in a range of 10 – 16.67, % v/v) under different percentages of THF (8.33, 16.67, 25 and 33.33, % v/v) in order to establish the recovery of the target compounds against the equilibrium solution. Figure 3 shows the recoveries of analytes (BPA, BPF, BPS, BPS-MAE, D-8 and TGSA) for each amphiphile using 120 µL of amphiphile (10% v/v).

Considering the alkyl chain length, recoveries decreased with an increasing number of carbon atoms. Although 1-octanol had similar recoveries than 1-hexanol for some analytes, the latter provided good extraction efficiency in a wider polarity range. The higher recoveries with SUPRAS of shorter alkyl-chain length amphiphiles can be attributed to both strongest hydrogen bonds for extraction, as explained above, and smaller aggregate sizes offering a higher contact surface for binding the contaminants. As shown in Figure 3, the percentage of THF did not influence recoveries so significantly in the tested range. SUPRAS volumes increased exponentially with the THF percentage (see Table S1), so that the concentration factor also dropped. For this reason, an intermediate value of 16.67% v/v THF was set as optimal for further experiments.

Once the optimal amphiphile and THF percentages were selected, we evaluated different volumes of 1-hexanol to form the SUPRAS. Recoveries were expected to increase with the percentage of amphiphile and concentration factors to decrease linearly (as SUPRAS volumes increased). Experiments were carried out in the presence of dust (50 mg) with SUPRASs formed with 120, 150 and 200 µL of amphiphile (10, 12.5 and 16.67% v/v, respectively). Recoveries were maximal with 200 µL of 1-hexanol and were of 93 ± 3 for BPA, 77 ± 4 for BPS, 88 ± 2 for BPF, 80 ± 2 for D-8 and 82 ± 3 for TGSA. These values were just slightly lower than without dust at the same 1-hexanol percentage (see figure S1). Under these conditions the SUPRAS volume extract was of 207 µL (calculated as specified in Table S1).

3.2. Analytical performance and validation

Calibration curves were prepared in SUPRAS (10 – 10,000 $ng \cdot g^{-1}$, n=11, 5,000 $ng \cdot g^{-1}$ of IS mix). As can be seen in Table 3, the correlation coefficients were in the range 0.9597

– 0.9993. Method detection (MDL) and quantification (MQL) limits were estimated considering a signal to noise ratio of 3 and 10, respectively, and were in the range 0.5 – 10 and 1 – 20 $ng \cdot g^{-1}$, respectively.

Calibration curves were also run in the presence of two dust samples (mix dust and SRM Baghouse dust) at two sample sizes (25 and 50 mg) to validate the methodology at the same spiking levels (10 – 10,000 $ng \cdot g^{-1}$, *n*=11). Matrix effects were calculated as the ratio from both slopes ($SUPRAS_{with\ dust}$/SUPRAS x 100) and were acceptable and in the ranges 70 – 100% and 86-120% for the dust mix and the SRM, respectively, at 25 mg, so that this sample size was considered as optimal. Correlation coefficients were in the range 0.9651 – 0.9961 and 0.9915 – 0.9995 for the dust mix and the SRM, respectively. SUPRAS blanks and unfortified dust samples did not contain detectable levels of the target compounds.

3.3. Extraction of bisphenols in real samples.

Ten indoor dust samples collected from different public environments and they were analyzed by the validated SUPRAS method. Table 4 shows the concentration range, mean, median and detection percentages for each analyte. In Table S2 the concentrations of the target compounds and the IS recoveries in each sample is specified. IS recoveries varied in the ranges 71 – 108 and 69 – 95% for BPA-d_6 and BPS-d_8, respectively. BPA was the most abundant bisphenol detected in all the samples, with a mean of 1,883 $ng \cdot g^{-1}$ followed by BPS (203 $ng \cdot g^{-1}$) and BPF (70 $ng \cdot g^{-1}$), which are their most used analogs in the industry. These concentrations are well in agreement with those reported in other countries (see Table S3). For example, concentrations for BPA in the literature ranges from 630 to 3,260 $ng \cdot g^{-1}$ (median) (Liao et al., 2012) and from 100 to 3,800 $ng \cdot g^{-1}$ (mean) (Wang et al., 2015); for BPF ranges from 38 to 450

310 ng·g^{-1} (median) (Liao et al., 2012) and from 1.9 to 5,500 ng·g^{-1} (mean) (Wang et al.,
311 2015) and for BPS ranges from 170 to 810 ng·g^{-1} (median) (Liao et al., 2012) and from
312 <2 to 1,500 ng·g^{-1} (mean) (Wang et al., 2015). In this study levels were in the ranges
313 192 – 4,444 ng·g^{-1}, 29 – 183 ng·g^{-1} and <0.075 – 736 ng·g^{-1} for BPA, BPS and BPF,
314 respectively.

315 Emerging BPA replacements (BPS-MAE, D-8 and TGSA), which are for the
316 first time reported in this study, were detected in 50%, 70% and 90% of the dust
317 samples, respectively. They were less abundant than BPS and BPF, with medians
318 between 6 and 22 ng·g^{-1} (around ten-fold lower values). This suggests that they are
319 used in lower amounts or in fewer types of materials or that their migration is slower
320 than that of the other bisphenols. We could not find information about other uses than
321 thermal paper.

322

323 **4. Conclusions**

324 The emerging BPA replacements (BPS-MAE, D-8 and TGSA) were detected for
325 the first time in indoor dust, at median levels around ten times lower than BPS but
326 frequently detected (50 – 90%). These replacements have previously been reported as
327 colour developers in thermal paper. The SUPRAS method is suitable as generic sample
328 treatment of indoor dust, the procedure was simple and fast (5 min stirring + 20 min
329 centrifugation), recoveries were within the required levels (69 – 108%) and LODs were
330 satisfactory for this matrix (in the low ng·g^{-1}). Results show the potential of these
331 emerging contaminants to migrate into the environment and constitute a first insight
332 into their presence in indoor dust as a relevant route of exposure. It is worthy to monitor
333 these compounds in future studies taken into account the limited number of samples and
334 the fact that they seems to be frequently present, specially taken into account that they

are considered toxic (TGSA, D-8) and very toxic (BPS-MAE) to aquatic life according to the data available on the ECHA database.

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FIGURE CAPTIONS

Figure 1. Schema of SUPRAS method for the determination of emerging BPA replacements in indoor dust samples.

Figure 2. Schema of the synthesis of the SUPRAS made up of 1-hexanol in THF:water mixtures, which involves processes of self-assembly and coacervation.

Figure 3. Extraction efficiency of target compounds with SUPRAS based on amphiphiles of different alkyl chain length (C6, C8 and C10) under different percentages of THF and expressed as mean ± SD (*n*=3). Conditions: blanks (dust: 0 mg), concentration of amphiphile (10% v/v), concentration of THF (8.33 – 33.33, % v/v), final volume of 1.2 mL.

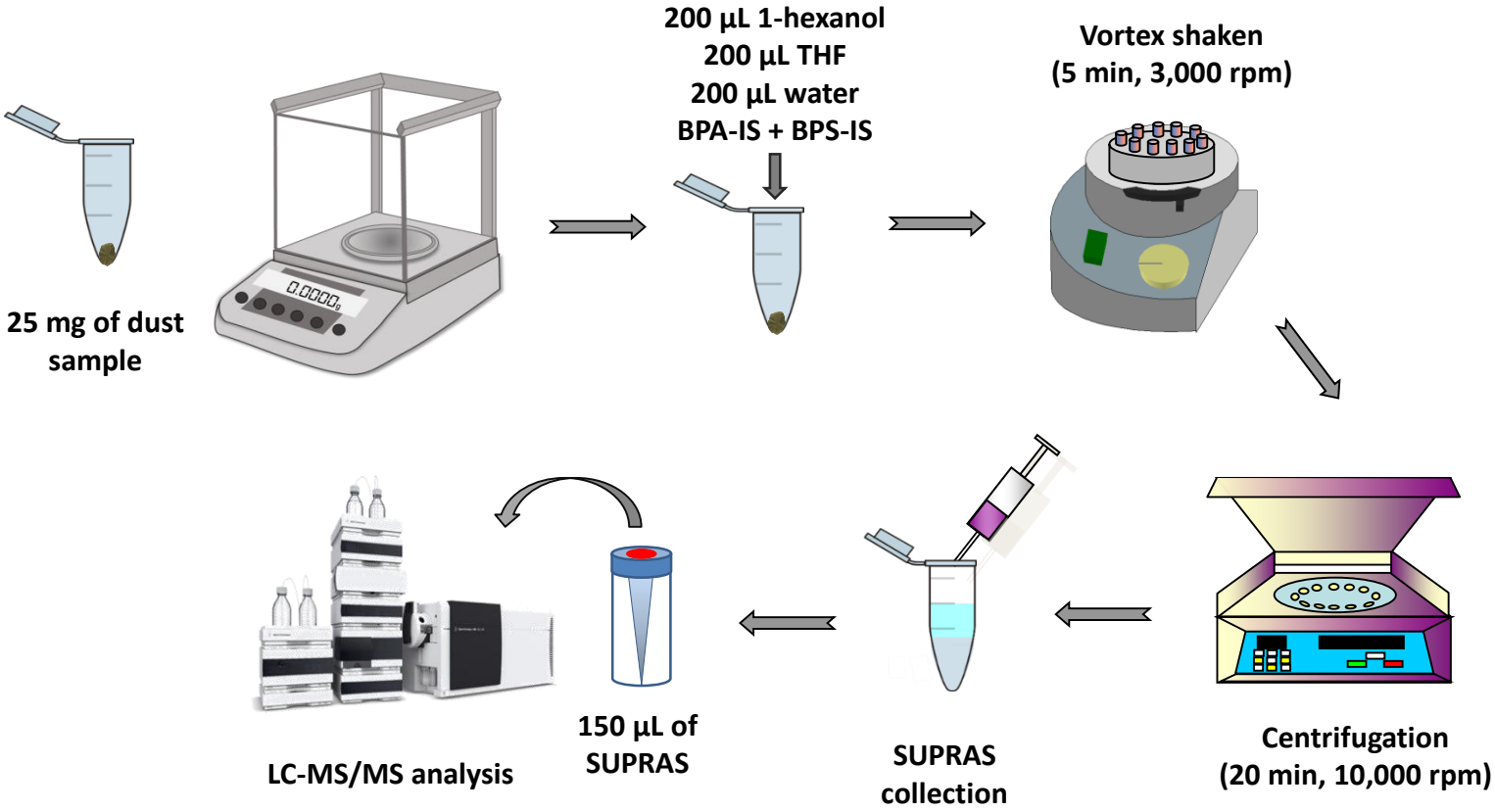

25 mg of dust sample
200 µL 1-hexanol
200 µL THF
200 µL water
BPA-IS + BPS-IS
Vortex shaken
(5 min, 3,000 rpm)
Centrifugation
(20 min, 10,000 rpm)
SUPRAS collection
150 µL of SUPRAS
LC-MS/MS analysis

Figure 1

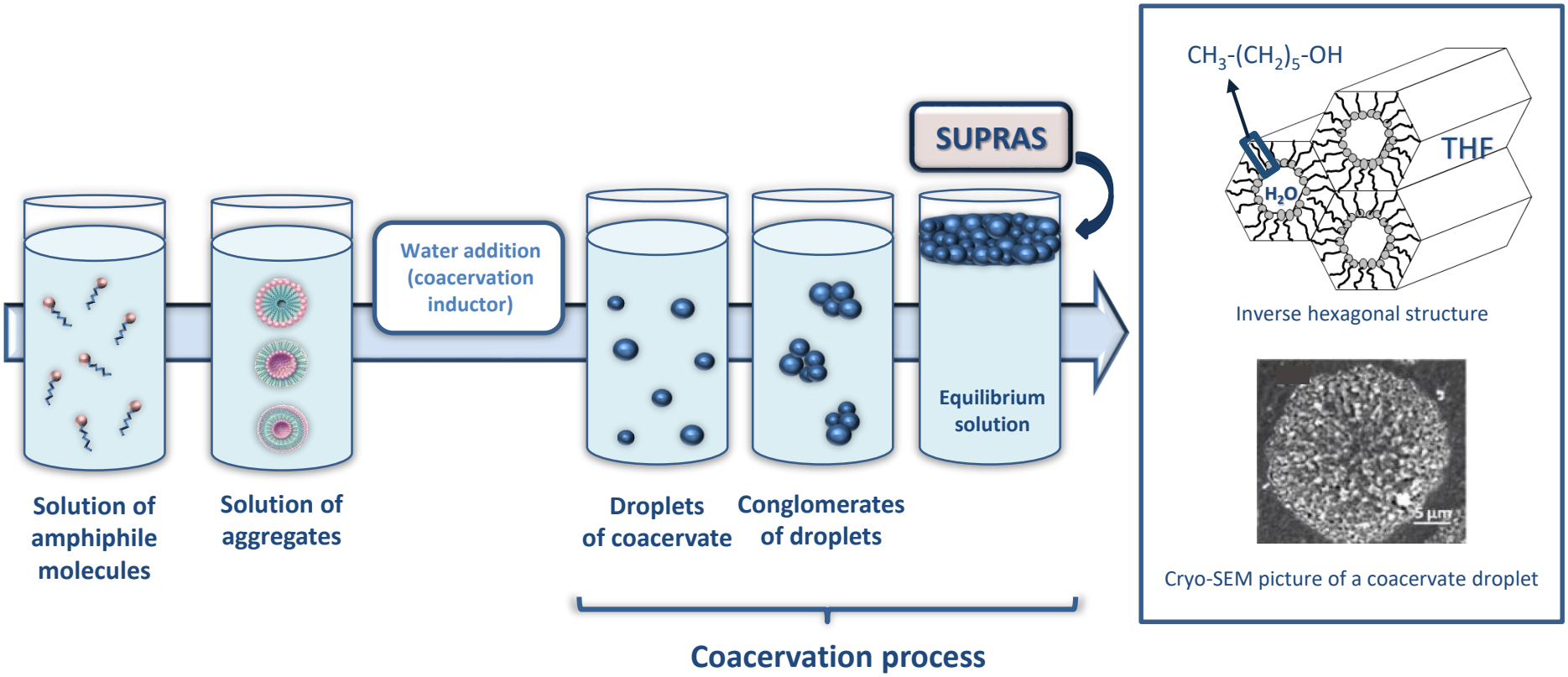

SUPRAS
Water addition (coacervation inductor)
Solution of amphiphile molecules
Solution of aggregates
Droplets of coacervate
Conglomerates of droplets
Equilibrium solution
Coacervation process
CH_3-$(CH_2)_5$-OH
THF
H_2O
Inverse hexagonal structure
5 µm
Cryo-SEM picture of a coacervate droplet

Figure 2

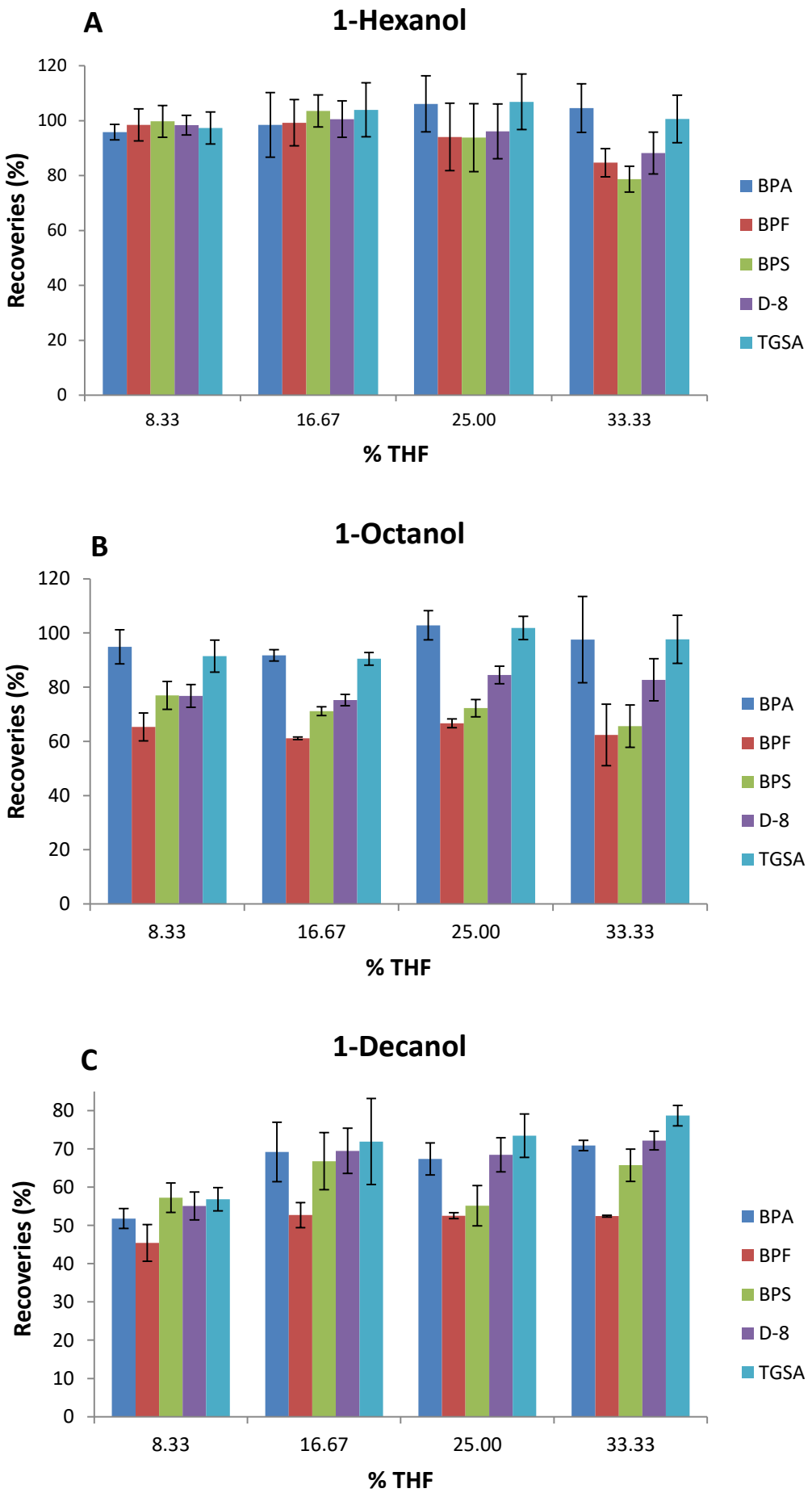
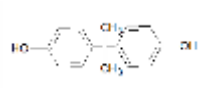
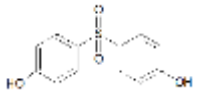
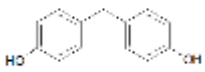
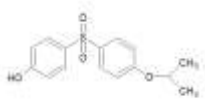
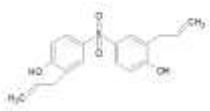
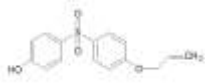

A
1-Hexanol
Recoveries (%)
120
100
80
60
40
20
0
8.33
16.67
25.00
33.33
% THF
BPA
BPF
BPS
D-8
TGSA
B
1-Octanol
Recoveries (%)
120
100
80
60
40
20
0
8.33
16.67
25.00
33.33
% THF
BPA
BPF
BPS
D-8
TGSA
C
1-Decanol
Recoveries (%)
80
70
60
50
40
30
20
10
0
8.33
16.67
25.00
33.33
% THF
BPA
BPF
BPS
D-8
TGSA

Figure 3

Table 1. Compound name and CAS number, molecular structure, chemical formula, monoisotopic mass and log P of BPA, BPS, BPF, BPS-MAE, D-8 and TGSA

Compound & CAS	Molecular structure	Chemical formula	Monoisotopic mass (g/mol)	Log P
4,4'-(propane-2,2-diyl) diphenol (BPA) ***80-05-7***		$C_{15}H_{16}O_2$	228.115	3.32[a] 3.3[b]
4,4'-Sulfonyldiphenol (BPS) ***80-09-1***		$C_{12}H_{10}O_4$	250.030	1.9[b]
4,4'-Methylenediphenol (BPF) ***620-92-8***		$C_{13}H_{12}O_2$	200.084	2.91[a] 2.9[b]
4-(4-propan-2-yloxyphenyl) sulfonylphenol (D-8) ***95235-30-6***		$C_{15}H_{16}O_4S$	292.077	3[b]
4-(4-hydroxy-3-prop-2-enylphenyl)sulfonyl-2-prop-2-enylphenol (TGSA) ***41481-66-7***		$C_{18}H_{18}O_4S$	330.093	4.1[b]
4-((4-(Allyloxy)phenyl)sulfonyl)phenol (BPS-MAE) ***97042-18-7***		$C_{15}H_{14}O_4S$	290.0607	2.9[b]

LogP values obtained from PubChem, [a]experimental, [b]calculated

Table 2. MRM transitions, dwell time, fragmentor voltage and collision energy. Quantifiers for target compounds are indicated in bold

Compound	Precursor ion (m/z)	Product ion (m/z)	Dwell time (ms)	Fragmentor (V)	Collision energy (eV)	Polarity
BPA	**227.1**	**212.2**	**50**	**100**	**20**	Negative
BPA	227.1	113.0	50	100	24	Negative
BPF	**199.0**	**105.0**	**50**	**100**	**25**	Negative
BPF	199.0	93.0	50	100	30	Negative
BPS	**249.0**	**108.0**	**50**	**100**	**20**	Negative
BPS	249.0	92.1	50	100	32	Negative
BPS-MAE	**289.1**	**248.1**	**50**	**100**	**20**	Negative
BPS-MAE	289.1	184.1	50	100	30	Negative
D8	**291.1**	**248.0**	**50**	**100**	**25**	Negative
D8	291.1	184.1	50	100	25	Negative
TGSA	**329.1**	**132.1**	**50**	**100**	**25**	Negative
TGSA	329.1	148.1	50	100	25	Negative

Table 3. Analytical performance of the SUPRAS-based calibration[a]

	Slope (ua g·ng^{-1}) ± Error	Lineal range (ng·g^{-1})	R^2	LOD (ng·g^{-1})	LOQ (ng·g^{-1})
BPA	0.000151 ± 3·10^{-6}	20-10,000	0.9977	10	20
BPS	0.0020 ± 0.0001	2-10,000	0.9872	1	2
BPF	0.000081 ± 2·10^{-6}	20-10,000	0.9962	10	20
D8	0.012 ± 0.001	2-10,000	0.9597	1	2
TGSA	0.0015 ± 0.0001	2-10,000	0.9759	1	2
BPS-MAE	0.00309 ± 3·10^{-5}	1-10,000	0.9993	0.5	1

[a]IS mix at 5,000 ng/g, *n*=11, weight 1/x, origin included

Table 4. Concentration of target compounds (in ng·g^{-1}) found in indoor dust samples from different public microenvironment in Spain (*n*=10)

	BPA	BPF	BPS	BPS-MAE	D8	TGSA
Concentration range	192 - 4444	Detected - 183	n.d. - 736	n.d. - 79	n.d. - 58	n.d. - 48
Mean[a]	1883	79	290	20	23	22
Median[b]	1739	60	193	6	20	22
Detection percentage (%)	100	100	70	50	70	90

n.d.: non-detected

[a]: Calculated without values below the LOQ

[b]: Calculated without values below the LOQ