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Abstract: A new analytical method was optimized to determine 18 disinfection by-products (DBPs) in drinking water, including four different chemical groups. For this purpose, spiral-shaped hollow-fibre liquid phase microextraction with 1-octanol as the acceptor solvent assisted by effervescence was applied using a homemade supporting device that was specifically designed for this application. The device was printed in a 3D printer and allows for an increased fibre surface even with a low sample volume, which significantly facilitates the extraction. The samples were analysed by gas chromatography coupled to both an electron capture detector and a mass spectrometer for the quantification and unequivocal identification of the analytes, respectively. Effervescence was generated using citric acid and bicarbonate at a molar ratio 1:2, which significantly improves the extraction efficiency and reduces mechanical operations, since stirring and modifiers are not required. The results showed enrichment factors ranging from 13.1 to 140.1. Satisfactory recoveries (80-113 %) were obtained, with relative standard deviations from 3 to 15 % and good linearity. The detection limits (ng L-1) ranged from 10 to 35 (trihalomethanes), 12 to 220 (halonitromethanes), 17 to 79 (haloacetonitriles) and 10 to 16 (haloketones). The applicability of the method was assessed in 6 local water distribution systems.

Effervescence-assisted spiral hollow-fibre liquid-phase microextraction of trihalomethanes, halonitromethanes, haloacetonitriles, and haloketones in drinking water

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Abstract

A new analytical method was optimized to determine 18 disinfection by-products (DBPs) in drinking water, including four different chemical groups. For this purpose, spiral-shaped hollow-fibre liquid phase microextraction with 1-octanol as the acceptor solvent assisted by effervescence was applied using a homemade supporting device that was specifically designed for this application. The device was printed in a 3D printer and allows for an increased fibre surface even with a low sample volume, which significantly facilitates the extraction. The samples were analysed by gas chromatography coupled to both an electron capture detector and a mass spectrometer for the quantification and unequivocal identification of the analytes, respectively. Effervescence was generated using citric acid and bicarbonate at a molar ratio 1:2, which significantly improves the extraction efficiency and reduces mechanical operations, since stirring and modifiers are not required. The results showed enrichment factors ranging from 13.1 to 140.1. Satisfactory recoveries (80-113 %) were obtained, with relative standard deviations from 3 to 15 % and good linearity. The detection limits (ng L^{-1}) ranged from 10 to 35 (trihalomethanes), 12 to 220 (halonitromethanes), 17 to 79 (haloacetonitriles) and 10 to 16 (haloketones). The applicability of the method was assessed in 6 local water distribution systems.

Keywords

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1. Introduction

The disinfection of public drinking water is essential to preserve human health. However, toxic substances can also be formed during disinfection, i.e., disinfection by-products (DBPs), to which almost the entire population is exposed to different degrees [1,2]. DBPs were first described in 1974 [3] and have been studied for over 40 years. The most common DBPs worldwide are trihalomethanes (THMs) and haloacetic acids (HAAs), which are typically used as markers in water. The most important health risk of THMs is cancer, which has been demonstrated to increase after chronic exposure [4]**.** For this reason, the European Union and the US Environmental Protection Agency (US EPA) have established 80 and 100 µg L^{-1} as the maximum concentrations of THMs and HAAs in drinking water, respectively [2].

Currently, several analytical approaches have been developed to identify the THMs in drinking water, which are usually based on gas chromatographic separation of analytes followed by electron capture (ECD) and/or mass spectrometry (MS) detection. Generally, ECD provides lower detection limits for halogens containing molecules, but unequivocal confirmation is only possible by MS [5]. Regarding sample treatment procedures, several different techniques have been satisfactorily applied to the analysis of drinking water, including liquid-liquid extraction (LLE) with GC-MS and GC-ECD [5], headspace liquid-liquid micro extraction (LPME) with GC-ECD [6], hollow fibre LPME with GC-µECD [7], and solid phase microextraction (SPME) with GC-MS [8].

Nitrogenous disinfection by-products (N-DBPs) are another chemical group of DBPs that can also be generated as a consequence of water disinfection processes, and they include a variety of chemical sub-groups, including haloacetonitriles (HANs) and halonitromethanes (HNMs) [1]. The occurrence of N-DBPs in drinking water is important because they are one of the most genotoxic and cytotoxic groups of DBPs [9]. Their toxicity derives from the high biological reactivity of their nitro group, especially in the case of bromonitromethane (BNM) and trichloronitromethane (TCNM), which increases the electrophilic character and leads to covalent bonds with various proteins, DNA and other nucleophiles within the body [10]. Moreover, the bromide containing nitromethanes are more genotoxic than the chlorinated analogues [11]. The World Health Organization (WHO) [12] has thus established that the recommended values for dichloroacetonitrile (DCAN) and dibromoacetonitrile (DBAN) in drinking water are 20 and 70 µg L^{-1}, respectively, while the EPA established levels of 6 and 20 µg L^{-1} of DCAN and DBAN, respectively [13].

N-DBPs can be formed during oxidation and disinfection of water, such as chlorine, chloramine, ozone-chlorine or ozone-chloramine treatments. The ozonation before chlorination can dramatically enhance HNM formation [14]. The sum of the analysed HNMs and HANs represented 3 % and 1 %, respectively, of the THMs in the US from 2000 to 2007. The formation of HNMs has not been proven to be correlated with that of THMs [9], and their levels in drinking water are generally lower than those for HANs (typically <5 μg L^{-1}), but they increase in chlorine or chloramine procedures that are preceded by ozonation [15,16].

The conventional method for HANs and HNMs determination is the US EPA Method 551, which is based on LLE and GC-ECD [17–19] and, most recently LLE and GC-MS with a programmable temperature injector for the analysis of 25 N-DBPs (HAAs, HNMs, and HANs) in drinking water [20]. Another method widely used for the determination of these compounds is extraction by SPME and the analysis by GC-ECD and/or GC-MS [21–23], as well as single-drop microextraction (SDME) in the static headspace mode followed by GC-MS for the determination of HNMs [24].

Haloketones (HKs) are a group of non-regulated volatile DBPs that can be formed in drinking water after several treatment processes, including ozone-chlorine, chlorine dioxide, chloramines and chlorine [25]. Among the HKs present in drinking water, the most common have been dichloroacetones (1,1- and 1,3-dichloroacetone, DCA) and 1,1,1-trichloroacetone (TCA) [26,27]. Moreover, and due to the volatile character of some DBPs, such as HKs and THMs, dermal absorption is another route of exposure that also contributes to the received dose [28]. Although HKs have been found to be carcinogenic and mutagenic, there is no regulated upper limit for HKs in drinking water [26].

The first method to identify the HKs in drinking water was proposed by the US EPA (method 504.1) and allows for the identification of VOCs (1,1-dichloroacetone and 1,1,1-trichloroacetone) by using LLE followed by GC-ECD [29]. More recently, drinking water has been analysed for for HKs, HANs, THMs, chloral hydrate and chloropicrin using HS-SPME/GC, LLE coupled to GC-ECD and MS, purge-and-trap followed by GC-MS and HS-GC-MS [4,28]. Recently, micro liquid–liquid extraction (MLLE) has also been applied to identify DBPs, including HANs, HKs and THMs [30–32], as well as headspace solid-phase microextraction (HS-SPME/GC-ECD) and SPME to identify HANs, HNMs and TCNM [24,33]. Using this method, Serrano *et al*. identified 14 HKs in treated water [34] providing lower limits of detection (LODs) than those achieved by EPA 504.1. However, it is worth noting that SPME presents several drawbacks, such as poor reproducibility, the low capacity of the extraction derived from the small amount of sorbent, and memory effects [35].

In this paper, hollow-fibre liquid phase microextraction (HF-LPME) has been used to extract DBPs from drinking water samples. This technique is simple to use and operate [36], and it is based on the principle of the supported liquid membrane, where the acceptor phase is separated from the donor phase. Compared with traditional extraction techniques, HF-LPME has several attractive features, such as its robustness, simple equipment requirement, low cost, enhanced capability related to a higher superficial area for the extraction, and reduced risk of cross-contamination and carryover effect due to the disposable nature of the fibre [37]. However, the main shortcomings are the assembly miniaturization and the lack of commercial prototypes [38]. To overcome these problems, it is possible to use 3D printing technology, which allows mass scale digital manufacturing at a low cost. These technologies are already used for other purposes, as well as for high-value scientific instruments [39]. The polymers currently used for the manufacturing of pieces in 3D printing based on the RepRap project are acrylonitrile butadiene styrene [40] and polylactic acid [41].

Additionally, the application of effervescence to assist in the dispersive micro-solid phase extraction was developed to simplify the extraction of volatile or semivolatile compounds, as well as to increase selectivity [42]. By means of the effervescence formed by CO_2 gas bubbles, volatile analytes move from the donor phase (liquid) to the acceptor phase (gas), which avoids or reduces heating the sample. This favours selectivity, as only volatile or semivolatile compounds can be recovered at low temperature. Moreover, the turbulence produced in the liquid by the formation of the bubbles favours natural agitation, which then avoids or reduces the need for mechanical agitation and minimizes the extraction time [43].

The main focus of this work was the optimization of a new method to extract eighteen DBPs (including THMs, HNMs, HANs and HKs) by using spiral-shaped hollow-fibre liquid phase microextraction (SHF-LPME) assisted by effervescence (EA). To the best of our knowledge, this is the first work that reports HF-LPME to extract HNMs, HANs and HKs. To facilitate the extraction, a device to support the spiral-shaped arrangement of the fibre was printed by a 3D printer. The extracts obtained by SHF-LPME were analysed by GC-µECD and GC–MS for quantification at low detection limits and unequivocal identification of the analytes. The new method has been applied to drinking water supplied from six water distribution systems that use different treatment processes.

2. Material and methods

2.1. Reagents and materials

All the target analytes, as follows, were of high purity, i.e., between 85 % and 99.5 % and were purchased from Supelco, Sigma-Aldrich (Ballefonte, USA): bromonitromethane (BNM), trichloronitromethane or chloropicrin (TCNM), bromoacetonitrile (BAN), chloroacetonitrile (CAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), 1,3-DCA and 1,1,1-TCA. A THMs mixture (200 µg/mL of each compound) was also purchased from Supelco, Sigma-Aldrich (Bellefonte, USA);

chloroform, bromodicloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM) and 1,2 dibromopropane, used as the internal standard, were purchased from Supelco, Sigma-Aldrich. Chloronitromethane (CNM), dibromonitromethane (DBNM), bromochloronitromethane (BCNM) and dichloronitromethane (DCNM) were purchased from Cansyn Chemical Corporation (Toronto, Canada). N-Octanol was purchased from Merck (Barcelona, Spain) and toluene, n-hexane, acetone, tert-butyl methyl ether (MTBE), sodium sulfate, and sulfuric acid were supplied from Teknokroma (Barcelona, Spain). Ultrapure water at 18 MΩ/cm (Millipore, Watford, UK) was used throughout the research work.

2.2. Standard solutions

Standard stock and intermediate solutions of each DBP were prepared in methanol at 2000 and 10 mg L^{-1}, respectively. The internal standard, 1,2-dibromopropane, was dissolved in methanol (5 mg L^{-1}) to achieve a final concentration of 5 µg L^{-1}. All the working solutions were prepared daily at 20 µg L^{-1} in ultrapure water and stored in darkness at -20 ºC for up to one month.

2.3. Sampling and sample preparation

Fourteen sampling points were taken from the following six drinking water distribution systems (DS) located in Huelva (Andalusia, Southwest of Spain): DS (1) Aljaraque, DS (2) Lepe, DS (3) Tinto, DS (4) Riotinto, DS (5) La Palma and DS (6) Andévalo. Four of the DSs include water from water treatment plants (WTPs) with advanced treatment processes using oxidation by pre-ozonation and adsorption by granular active carbon (Alj WTP 1, Lep WTP 2, Lpa WTP 5, and Tin WTP 3). The other two samples from WTPs (Rti WTP 4 and WTP 6) include water from locations 4 and 6 but with conventional treatment processes (absence of adsorption). Furthermore, water samples were also collected from the following drinking water reservoirs located downstream of each DS: (RSB (1), RAY (2), MOG (3), BEA (3), RZL (4), FLC (4), RBL (5) and RTH (6)). The sampling points corresponding to the different water DSs are illustrated in Figure 1 and Table S1 in the supplementary material.

The sample collection was carried out following the previously published procedure [7]. The stability of the compounds was studied, and the results revealed that the compounds are all stable for one week when stored at 4ºC, except for dibromonitromethane, which is only stable for one day [21,44].

2.4. SHF-LPME procedure

2.4.1 Extraction of DBPs using an assembly device made by 3D printing for SHF-LPME

The homemade SHF-LPME device designed for the extraction of DBPs is illustrated in Figures 2 and S1 in the supplementary material. The organic acceptor phase was supported by a porous Accurel Q 3/2 polypropylene hollow-fibre (Wuppertal, Germany) with the following dimensions: an internal diameter of 600 µm, a wall thickness of 200 µm, and 0.2 µm pores. The device was produced by 3D printing several pieces that were then assembled and for which there are two modes of operation: on headspace (HS) or direct extraction (DE). The pieces were designed using the CAD/CAM (Computer Aided Design/Computer Aided Manufacturing) technique. An open source 3D printer, Prusa i3, was used (see Figure S1A in the supplementary material). The material used to make the pieces was white polylactic acid (PLA).

The fibres were cut into 10 cm length fragments, and they were cleaned to remove any possible contaminant by immersing them in acetone for 5 minutes. Later, the fibres were air-dried for two minutes. When the fibres were dry, the different pieces of the device were assembled. As seen in Figure 2, the device is composed of five pieces, and the system works by introducing the needle through the holes of the pieces - 1 (cap septum), 2 (septum), 3 (stopper piece), 4 (hollow fibre positioner) and 5 (closure piece). The protruding needle tip is inserted into one end of the hollow fibre. The other end of the fibre is inserted into the hole of the piece 5 (closure piece). Then, piece 5 is turned until the fibre is wound around piece 4 (the hollow fibre positioner). Figure S1B shows the point-by-point description of the fibre arrangement on the support.

Next, the device with the hollow fibre is introduced in the acceptor phase (1-octanol) for 2 minutes to open the pores. The immersion of the fibre into the solvent also makes it more flexible, allowing it to be more easily wound without kinking. Then, the lumen of the membrane is flushed and filled with 1 mL of octanol by syringe to avoid bubbles. The total volume inside the 10 cm piece of fibre is 20 µL of octanol. Subsequently, the end of the fibre is plugged with a needle tip or by pressure with flat-tipped tweezers.

Before the SHF is introduced into the 20 mL vial containing the donor sample solution, several reagents were added as follows. The water samples (8 mL) were adjusted to pH 3 with 0.1 M of sulfuric acid (9.37 µL sulfuric acid, 0.1 M/mL sample). Sodium sulfate (300 mg/mL sample) was added to increase the extraction efficiency of the DBPs. A solution (1.2 g) containing a 2-fold molar concentration of sodium bicarbonate and citric acid was introduced into the vial containing the donor sample to produce agitation from effervescence; then, a hermetic closure was ensured by inserting the plug into the end of the fibre. The extraction of the target DBPs from the headspace was performed over a period of 30 minutes at 45 ºC. Once the extraction process was completed, the supporting device holding the hollow fibre was removed from the vial, the plug was removed from the end of the fibre, and the extract was collected from the lumen into 1.5 mL vials with inserts of 250 µL. Finally, 1 µL of the obtained extract was injected into the injection port of the GC-µECD.

2.5. Instrumentation analysis

The extracts were analysed by GC coupled to a ^{63}Ni micro-cell electron capture detector model 6890N (GC-µECD) (Hewlett Packard, Wilmington, USA). A DB-5MS column (30 m x 0.25 mm x 0.25 µm, Agilent Technologies) was used. The chromatographic conditions were as follows: split at a 1:10 ratio (12 mL min^{-1}); carrier gas, helium at column flow rate of 1 mL min^{-1}; and the injector temperature was 170 ºC. The oven temperature was optimized and programmed at an initial temperature of 35 ºC with a hold time of 2 min, raised to 65 ºC at a rate of 2 ºC/min with a hold time of 1 min, and finally increased to 180 ºC at 20 ºC/min for 2 min (the total runtime was 34 minutes). The detector temperature was set to 280 ºC with a nitrogen make-up gas flow-rate of 60 mL min^{-1}.

The extracts were also analysed in a GC-MS model ITQ 900 equipped with an ion trap analyser (Thermo Fisher Scientific, Rodano, Milan, Italy). Electron impact ionization (EI) at 70 eV and the SIM mode were used in the MS detector. The chromatographic column was a DB-5MS (30 m x 0.25 mm x 0.25 µm.) supplied by Agilent Technologies. The GC conditions were the same as described above for the GC-µECD. The transfer line and ion source temperatures were set to 170 ºC and 225 ºC, respectively [24]. The identification of DBPs was performed by comparison with the retention times of the corresponding standards and mass spectra. The ions selected to identify and quantify DBPs, which were selected for the NIST Mass Spectral Library, are shown in Table 1.

3. Results and discussion

3.1. Design of a device made with a 3D printer for SHF-LPME

The HF-LPME technique presents mechanical difficulties, especially when reduced sample volumes are used and longer fibres are needed to increase the extraction efficiency. To overcome this problem, a spiral-shaped hollow fibre arrangement can be used (SHF-LPME), but a specific supporting device is required to obtain a reproducible process and guarantee the spiral shape of the fibre.

To this end, the device, which was produced with a 3D printer, used in this work to assemble the SHF-LPME (Figure 2 and S1 in the supplementary material) overcomes these problems. The simple fibre handling, the reproducibility and extraction efficiency represent important improvements in comparison with other techniques based on the use of syringe needles. Figure 3 illustrates the comparison between the spiral- *vs* U-shaped HF and shows the following important advantages of the former: (i) a larger fibre surface for the extraction and a lower sample volume are required when compared to the U- or I-shaped HF; (ii) the possibility of performing the extraction in headspace mode (HS), even with high fibre lengths and low sample volume; (iii) good reproducibility due to the absence of contact between the fibre and the surface of the vial when using mechanical agitation or effervescence, even with long fibre lengths; (iv) the fibre attachment reduces the variability caused by vibrations when using mechanical agitation or effervescence; (v) good repeatability is achieved by successive tests with the same conditions; and (vi) the fibre handling when attaching it to the device is easier than with other modes, which require the attachment to one or two syringes.

3.2. Optimization of DBP extraction.

The variables affecting the extraction of DBPs were examined by using samples of water fortified with 10 μg L^{-1} of DBP (each) and the internal standard (ISTD) – except for 1,2-dibromopropane, which was spiked at 5 μg L^{-1}. The extracts were analysed by GC-μECD followed by compound confirmation by GC-MS. The relative peak areas of each DBP to the ISTD were calculated after each experiment (n=3).

3.2.1. Effect of operating variables in the extraction process (SHF-LPME-GC/μECD), (mode without effervescence)

The following six solvents were checked for the extraction of the analytes: heptane, 1-octanol, n-hexane, toluene, 1-propanol, and ethyl acetate. The compatibility of the selected solvents with the plastic material (PLA) of the supporting device was checked beforehand by immersing a sample of PLA into each solvent for one week. The solvents evaluated have the characteristics required to be used as acceptor solvents in the hollow fibre extraction process [45,46]. The extractions were checked by using two HF modes, i.e., direct and headspaces. The results (relative peak areas=analyte peak area/internal standard peak area) are shown as percentages in Figure S2. The most efficient solvent is 1-octanol, and it provided the best recoveries for almost all the analytes when using the headspace mode. Consequently, these conditions were selected in the further experiments.

The choice of the optimal fibre length was a critical step because longer fibres increase the volume of the acceptor solvent contained within the fibre, producing an increase in the extraction efficiency until a maximum, while the efficiency decreases when diluted over this value [47]. The fibre length was varied from 3 to 12 cm, and the results are illustrated in Figure S3. It can be concluded that the best results were obtained with a length of 10 cm. Longer fibre lengths did not increase the relative peak areas; therefore, the length was set at 10 cm for further experiments.

The extraction efficiency at different temperatures (Figure 4A) and extraction times (Figure 4B) was studied in triplicate using 1-octanol as the acceptor solvent in intervals of 20 to 40 minutes (20, 30 and 40 minutes) and 35 to 70 ºC (35, 45, 60 and 70 ºC), respectively. The results shown in Figure 4A reveal that the extraction efficiency increased from 35 to 45 ºC but decreased at higher temperatures. Likewise, the best extraction time is in the range of 20-30 minutes, decreasing at 40 minutes. After analysing the results obtained, a temperature of 45 ºC and an extraction time of 30 minutes were used for further experiments.

Sample stirring was studied to accelerate the kinetics of the extraction [24]. The stirring speed was optimized in the range of 100 to 1500 rpm and was conducted with a magnetic stirrer. In general, up to 700 rpm, the relative areas of the studied analytes correspondingly increase with the stirring speed; however, with speeds between 700 and 1200 rpm, the relative areas did not increase significantly and decreased from 1500 rpm. Therefore, the selected stirring speed for further experiments was 700 rpm.

To improve the extraction efficiency, the pH of the sample should be adjusted to neutralize analytes, thus decreasing their solubility in the donor phase. The pH of the acceptor phase should allow the ionization of the analytes [48]. In this work, the sample pH was modified over the range of 3.0 to 7.0. A sulfuric acid solution at 0.1 mol L^{-1} was used for the pH adjustment of the aqueous sample. Figure 4C illustrates the pH effect in the extraction of DBPs using the hollow fibre. The results showed that the optimal pH ranged from 3.0 to 4.5. In addition, the extraction of volatile compounds in aqueous solutions can be enhanced by the presence of an organic modifier [49]. Thus, the addition of a chemical modifier, i.e., methyl tert-butyl ether (MTBE), in the sample favours the volatilization of HNMs, thus obtaining four-fold increased signals when compared with the absence of a modifier [43,50]. According to this criterion, the effects of two chemical modifiers (n-hexane and MTBE) on the efficiency of DBP extraction with HF-LPME were tested. Both n-hexane and MTBE were tested by adding 150-300 µL of each to the aqueous sample. The best results were obtained by adding 200 µl of MTBE (Figure 4D).

Finally, the addition of salt increases the ionic strength of the sample, which could enhance the extraction efficiency of the target DBPs in the organic phase. In this work, several experiments were carried out by adding sodium sulfate, i.e., from 100 to 400 mg salt/mL of sample. The highest peak areas of DBPs for most of the analytes were obtained with the addition of 300 mg of sodium sulfate per mL of sample (Figure 4D); therefore, this value was set for further experiments.

3.2.2. Effect of operating variables in the Extraction Process (EA-SHF-LPME-GC/µECD), (with effervescence mode)

Several factors were considered to evaluate the effect of effervescence, namely, the following: stability, time, absence of an insoluble organic modifier, and the amount of carbon dioxide. Several studies reported that the effervescent mixture of sodium bicarbonate and citric acid is more stable, and its effervescence time is longer [42,43,51]. Therefore, citric acid was selected as a proton donor, and sodium bicarbonate was selected as the carbon dioxide source. The molar ratio variation of the proton donor and the carbon dioxide source can affect the final pH of the sample, its effervescence time and viscosity, as well as the amount of CO_2 bubbles. Therefore, the molar ratios 1:1, 1:2 and 1:4 (citric acid:sodium bicarbonate) were checked. The results (Figure S4) indicated that the best extraction efficiency was obtained with molar ratios 1:1 and 1:2. Therefore, a compromise value was set with a molar relation 1:2 for further experiments.

Figure 5 shows the relative peaks areas of analytes after the extraction with and without effervescence, and with effervescence and a modifier. As seen, during the effervescence, CO_2 bubbles enhance the diffusion and avoid the necessity of a modifier. In subsequent experiments, it was verified that the addition of sodium sulfate to the sample improves the extraction efficiency. For this reason, a 300 mg sodium sulfate/mL sample was added in the further experiments. Likewise, a higher extraction efficiency was obtained with effervescence by adjusting the sample to a pH of 3 (Figure S5).

The amount of the effervescent mixture has an effect on the extraction efficiency since greater amounts generate additional carbon dioxide and maintain the effervescence for longer periods of time. However, if the weight of the effervescent mixture is too high, the overpressure produced by the excess CO_2 causes leaks of bubbles and adversely affects both the recovery and extraction efficiency, as tested at different temperatures and extraction times (Figure S6A). As seen in Figures S6B and S6C, the amount of the effervescent mixture was optimized from 0.8 to 1.6 g at different temperatures, and the extraction times and relative peak areas of the studied analytes increased until 1.2 g (effervescence time 13.6 min); however, the relative peak areas decreased at 1.6 g (effervescence time 18.6 min) (Figure 6SA). Thus, 1.2 g of the effervescence mixture was selected for use in further experiments.

Two other factors affecting the efficiency of the extraction are the temperature and the extraction time. Higher temperatures usually enhance effervescence, which in turn increases the extraction efficiency [52]. The effects of the temperature and extraction time in the extraction process were investigated at different temperatures (25 and 45ºC) and extraction times (10 and

30 min) (Figure S7). The extraction efficiency increases with the temperature. The most significant enhancement occurred with DCAN and BCAN, while the lowest occurred with TCM, BDCM and 1,1,1-TCA. After the experiments, the optimum temperature was determined to be 45 ºC. It was also found that increasing the contact time improves the extraction efficiency. In conclusion, the optimum extraction time for the extraction of the 18 DBPs was 30 minutes.

Finally, when using effervescence, constant stirring was not required and was only performed to assure the solubilization of the compounds before the extraction.

3.2.3. Comparison of the enrichment factors in HS-EA-SHF-LPME vs HS-SHF-LPME

The enrichment factor (E_e) of each analyte was checked using both analytical methods developed (HS-EA-SHF- *vs* HS-SHF-LPME-GC/μECD). The addition of reagents for the effervescence complicates the procedure, but the CO_2 bubbles during the effervescence also enhance the diffusion and avoid the necessity of a modifier. As discussed in section 3.2.2., the optimum amount of the effervescence mixture is 1.2 g, which led to an effervescence time of 13.6 min. This time is less than the extraction time (30 min), because higher amounts produce overpressure caused by the excess of CO_2, thus causing leaks of bubbles and decreasing the peak areas (Figure S6A). This fact could be a drawback when comparing effervescence with stirring. However, the effervescence effect improved the extraction in most of the analytes studied, and higher enrichment factors were obtained (Table 1). This is not the case for several THMs, because effervescence does not significantly improve their extraction. The E_e of the TCM was approximately 1.6-fold lower with effervescence assisted extraction and 1.2-fold lower for BDCM, but it was higher in the ranges of 1.2-1.3-fold for DBCM and TBM, respectively. Effervescence favoured extraction in most of the HNMs, with the exception of BNM and TCNM. For the other HNMs, significant increases of Ee were obtained - especially for CNM, whose response was 4.5-fold higher with effervescence. Effervescence significantly favoured the extraction of all HANs, obtaining Ee values from 4.5 to 12.1-fold. The main improvement of the effervescence method was observed in HKs, obtaining Ee values from 31.8 to 12.2-fold with effervescence extraction.

Thus, according to the results shown in Figure 6 and Table 1, effervescence favoured the extraction of TBM and DBCM, but not the extraction of TCM and BDCM. It also favoured the extraction of HNM compounds, except BNM and TCNM. The extraction efficiencies of HANs and HKs were significantly improved with the application of the effervescence effect.

3.3. Quality parameters of the extraction method

To evaluate the applicability of the optimized method (HS-EA-SHF-LPME followed by GC/µECD) with real samples, the quality parameters have been calculated in the drinking water from six WDSs in the Huelva area (Figure 1 and Table S1). To this end, the linearity, limits of detection (LODs) and quantification (LOQs), reproducibility and repeatability (both inter- and intra-day), recovery and enrichment factors were calculated. The quantification of the analytes was always performed using the µECD detector due to its higher sensitivity, while the MS detector was used only for the unequivocal identification of the analytes using the NIST database and SIM mode.

The linearity of the internal calibration curves was obtained using six levels, ranging from 0 to 60 µg L^{-1}, for each DBP by injections in triplicate. The linear ranges were 0.025 to 50 µg L^{-1} for regulated THMs, 0.1 to 30 µg L^{-1} for CAN, DCNM, CNM, BCNM and DBNM, 0.1 to 20 µg L^{-1} for 1.3 DCA, BAN and BNM, 0.1 to 40 µg L^{-1} for 1,1,1-TCA, DCAN, TCAN and BCAN, and 0.1 to 60 µg L^{-1} for DBAN and TCNM. The calibration curves showed good correlation coefficients ($0.098 < R^2 < 0.999$) for all the analytes.

The LODs and LOQs were calculated as the lowest analyte concentrations that correspond to a chromatographic signal/background noise (S/N) ratio of 3 and 10, respectively. The LOD values obtained were in the range of 10 to 35 ng L^{-1} for regulated THMs, 12 to 145 ng L^{-1} for the 6 HNMs, 17 to 79 ng L^{-1} for HANs, and 10 to 16 ng L^{-1} for the HKs studied. The LODs obtained with the new method are good for the 18 DBPs and they were far below the maximum concentration levels established. Thus, the LODs are three orders of magnitude lower than the US EPA established maximum concentrations for THMs (80 µg L^{-1} [2]), two for DCAN (6 µg L^{-1} [13]) and three for DBAN (20 µg L^{-1} [13]).

Compared with the previously reported LODs (Table S2), the detection limits for trihalomethanes are comparable to those obtained by other HP-LPME methods (which analyse only THMs) [7,53–55] but are higher than those obtained by liquid-liquid extraction followed by ECD [31] or MS/MS [5]. However, the LLE methods are time consuming and involve the use of higher amounts of organic solvents. Regarding the determination of HNMs [21,31,56,57], HANs [5,21,31,56,57] and HKs [5,31] by other methods reported in the literature, which has been analysed for the first time by HF-LPME in this work, this last method is the most sensitive for almost all the compounds (Table S2).

The precision was evaluated to determine the repeatability (extracting and analysing five samples of water on the same day) and reproducibility (extracting and analysing ten samples of water on three different days). In both cases, milli-Q water samples spiked at two concentrations (0.5 and 10 µg L^{-1}) of each DBP were used. The repeatability values obtained (0.5 µg L^{-1}), measured as the percentage of the relative standard deviation (% RSD), were from 5 to 10 % for THMs, 5 to 13 % for HNMs, 3 to 15 % for HANs, and 6 to 10 % for HKs. The reproducibility results ranged from 5 to 10 % for THMs, 6 to 12 % for HNMs, 5 to 16 % for HANs, and 6 to 10 % for HKs. The repeatability for THMs is comparable with other methods but is slightly worse than that obtained by graphite reinforced HF-LPME [55], as seen in Table S2. For four of the N-DBPs, the repeatability is better with methods that do not use HF-LPME [21,31,56–58], but it is comparable or better for others.

The extraction recovery was evaluated using tap water spiked with 0.5 and 10 μg L^{-1} of DBPs (each) in quintuplicate (n=5). These levels were selected according to their expected values in drinking water. As can be observed in Table 1, the recoveries of all DBPs ranged from 86 (at low level) to 104 % (at high level).

To probe the enrichment factor (E_e) obtained with our extraction, it was calculated as the analyte concentration in the acceptor phase (Ca) against the initial concentration in the sample (Cd), Ee = Ca/Cd [6]. Enrichment factors of 0.5 μg L^{-1} were calculated (Table 1), showing average values of approximately 45-fold, which is in good agreement with most of the Ee reported values. Likewise, a previous work reported enrichment factors in the range of 21-52 for three trihalomethanes and 62 for TBM using HF-LPME [7]. Other papers reported higher Ee factors, especially for TBM. Thus, N. Vora-adisak, *et al* obtained Ee values in the range of 28-62 for four trihalomethanes [54]. Higher enrichment factors can also be obtained for tribromomethane (51) and chlorodibromomethane (71) using a graphite-reinforced hollow-fibre membrane enrichment, as the Ee values obtained for the other halomethanes studied were approximately 40-48 [55]. However, these methodologies were optimized for a reduced number of compounds including only trihalomethanes, which allows good results to be obtained for the studied compounds.

3.4. Application of the proposed method to water samples from water distribution systems (WDS)

As described in section 2.3., the optimized method was used for the analysis of water samples obtained from six WDSs of Huelva (Spain). The analytical results obtained are shown in Table 2. The values of the THMs obtained were in the range of 15.9 (Andévalo WTP) to 55.2 μg L^{-1} (Riotinto WTP). The concentrations of THMs in the reservoirs were higher than that in the treated water of their source plant. The values ranged from 22.7 (Tharsis Reservoir) to 78.8 μg L^{-1} (Bollullos Reservoir). The increase of spatial variations was between 1.2 and 1.4 times with respect to the concentration in the WTP. Using the Pearson correlation method, a good correlation was found between the concentration of THMs with DOC (r: 0.704; p: 0.05), temperature (r: 0.510; p: 0.05), and UV_{254} (r: 0.807; p: 0.00). The concentrations and THM formation behaviour are in good agreement with other published works [7,59,60].

Several DBPs were detected by GC-μECD in the analysed samples, and the following results were obtained: BNM (0.49-3.43 μg L^{-1}), BCAN (0.19-2.07 μg L^{-1}), DBAN (not detectable-0.40 μg L^{-1}), DCAN (0.10-1.29 μg L^{-1}), and 1,3 DCA (0.98-1.02 μg L^{-1}). The concentrations of BNM, BCAN, DCAN and TCAN in the treated water from the WTPs are higher than those obtained in the corresponding reservoirs of the distribution systems, thus suggesting a possible degradation along the distribution system. The concentrations obtained are in good agreement with other published works [22,24,32,34]. A clear correlation of the formation of analysed HNs, HANs and HKs with the variables DOC, UV_{254}, pH or temperature (T) was not found.

4. Conclusions

A new method based on spiral-shaped hollow-fibre liquid phase microextraction assisted by effervescence (EA-SHF-LPME) was developed to extract 18 DBPs from 4 different chemical classes, THMs (4), HNMs (6), HANs (6) and HKs (2), from drinking water. This work describes the use of HF-LPME for the extraction of HNMs, HNMs and HKs, and the method allows their extraction with THMs from drinking water. Several important strategies have also been optimized, as follows: (i) extraction in the headspace mode, which allows a higher resolution to be obtained; and (ii) effervescence-assisted extraction, which increases the enrichment factors for several analytes up to 30-fold and simplifies the analysis by reducing mechanical operations, such as agitation, and avoiding the use of an MTBE. Moreover, a new plastic supporting device (polylactic acid PLA) was designed using a CAD/CAM system and was made using a 3D printer. This device improves the extraction of analytes from low volume liquid samples and enables the extraction process in repeatable conditions by assembling the fibre in a spiral shape. The method developed offers a reproducible process capable of reducing the potential errors produced in the laboratory due to the manual handling of fibres. Thus, our method proposed here enables the analysis of a wide variety of analytes, which facilitates the operations and opens up opportunities for further investigations using a miniaturized instrument designed with an SHF-LPME configuration. Finally, the proposed method allows low detection limits (~ng L^{-1}) and high recoveries for DBPs to be achieved.

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References

[1] R.C. Hansson, M.J. Henderson, P. Jack, R.D. Taylor, Iodoform taste complaints in chloramination, Water Res. 21 (1987) 1265–1271. doi:10.1016/0043-1354(87)90179-5.

[2] C.M. Villanueva, S. Cordier, L. Font-Ribera, L.A. Salas, P. Levallois, Overview of Disinfection By-products and Associated Health Effects, Curr. Environ. Heal. Reports. 2 (2015) 107–115. doi:10.1007/s40572-014-0032-x.

[3] J.J. Rook, Haloforms in Drinking Water, J. - AWWA. 68 (1976) 168–172. doi:10.1002/j.1551-8833.1976.tb02376.x.

[4] K. Gopal, S.S. Tripathy, J.L. Bersillon, S.P. Dubey, Chlorination byproducts, their toxicodynamics and removal from drinking water, J. Hazard. Mater. 140 (2007) 1–6. doi:10.1016/j.jhazmat.2006.10.063.

[5] A.D. Nikolaou, T.D. Lekkas, S.K. Golfinopoulos, M.N. Kostopoulou, Application of different analytical methods for determination of volatile chlorination by-products in drinking water, Talanta. 56 (2002) 717–726. doi:10.1016/S0039-9140(01)00613-0.

[6] M.E. Aydin, S. Tongur, G. Kara, Analyses of trihalomethans in Konya dirinking water network, in: 10th Int. Multidiscip. Sci. Geoconference EXPO - Mod. Manag. Mine Prod. Geol. Environ. Prot. SGEM 2010, 2010: pp. 405–413.

[7] A. Domínguez-Tello, A. Arias-Borrego, T. García-Barrera, J.L. Gómez-Ariza, Application of hollow fiber liquid phase microextraction for simultaneous determination of regulated and emerging iodinated trihalomethanes in drinking water, J. Chromatogr. A. 1402 (2015) 8–16. doi:10.1016/j.chroma.2015.05.020.

[8] Y. Bichsel, U. Von Gunten, Formation of iodo-trihalomethanes during disinfection and oxidation of iodide-containing waters, Environ. Sci. Technol. 34 (2000) 2784–2791. doi:10.1021/es9914590.

[9] T. Bond, J. Huang, M.R. Templeton, N. Graham, Occurrence and control of nitrogenous disinfection by-products in drinking water - A review, Water Res. 45 (2011) 4341–4354. doi:10.1016/j.watres.2011.05.034.

[10] K. Nepali, H.Y. Lee, J.P. Liou, Nitro-Group-Containing Drugs, J. Med. Chem. 62 (2019) 2851–2893. doi:10.1021/acs.jmedchem.8b00147.

[11] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. DeMarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research, Mutat. Res. - Rev. Mutat. Res. 636 (2007) 178–242. doi:10.1016/j.mrrev.2007.09.001.

[12] World Health Organization (WHO), Guidelines for drinking water quality, 2011. https://www.who.int/.

[13] U.S. Environmental Protection Agency, 2018 Edition of the Drinking Water Standards and Health Advisories Tables, Washington, D.C. (E.E.U.U), 2018. https://www.epa.gov/environmental-topics/water-topics.

[14] J. Hoigné, H. Bader, The formation of trichloronitromethane (chloropicrin) and chloroform in a combined ozonation/chlorination treatment of drinking water, Water Res. 22 (1988) 313–319. doi:10.1016/S0043-1354(88)90120-0.

[15] K.L. Simpson, K.P. Hayes, Drinking water disinfection by-products: An Australian

perspective, Water Res. 32 (1998) 1522–1528. doi:10.1016/S0043-1354(97)00341-2.

[16] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Sclimenti, G.D. Onstad, A.D. Thruston, Occurrence of a new generation of disinfection byproducts, Environ. Sci. Technol. 40 (2006) 7175–7185. doi:10.1021/es060353j.

[17] D. Munch, D. Hautman, United States Environmental Protection Agency, EPA Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents , and halogenated pesticides/ herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection, 1995. https://www.epa.gov/sites/production/files/2015-06/documents/epa-551.1.pdf (accessed 17 February 2020)

[18] D. Liew, K.L. Linge, C.A. Joll, A. Heitz, J.W.A. Charrois, Determination of halonitromethanes and haloacetamides: An evaluation of sample preservation and analyte stability in drinking water, J. Chromatogr. A. 1241 (2012) 117–122. doi:10.1016/j.chroma.2012.04.037.

[19] F.Q. Huang, M.Y. Ruan, J.D. Yan, H.C. Hong, H.J. Lin, Y.J. Xiong, An improved method for determining HNMs in drinking water, Water Sci. Technol. Water Supply. 13 (2013) 1257–1264. doi:10.2166/ws.2013.135.

[20] R.A.A. Carter, D.S. Liew, N. West, A. Heitz, C.A. Joll, Simultaneous analysis of haloacetonitriles, haloacetamides and halonitromethanes in chlorinated waters by gas chromatography-mass spectrometry, Chemosphere. 220 (2019) 314–323. doi:10.1016/j.chemosphere.2018.12.069.

[21] I. Montesinos, M. Gallego, Solvent-minimized extraction for determining halonitromethanes and trihalomethanes in water, J. Chromatogr. A. 1248 (2012) 1–8. doi:10.1016/j.chroma.2012.05.067.

[22] Q. Luo, X. Chen, Z. Wei, X. Xu, D. Wang, Z. Wang, Simultaneous and high-throughput analysis of iodo-trihalomethanes, haloacetonitriles, and halonitromethanes in drinking water using solid-phase microextraction/gas chromatography-mass spectrometry: An optimization of sample preparation, J. Chromatogr. A. 1365 (2014) 45–53. doi:10.1016/j.chroma.2014.09.003.

[23] F.R. Kermani, A.M. Tugulea, J. Hnatiw, V.H. Niri, J. Pawliszyn, Application of automated solid-phase microextraction to determine haloacetonitriles, haloketones, and chloropicrin in Canadian drinking water, Water Qual. Res. J. Canada. 48 (2013) 85–98. doi:10.2166/wqrjc.2013.012.

[24] I. Montesinos, M.J. Cardador, M. Gallego, Determination of halonitromethanes in treated water, J. Chromatogr. A. 1218 (2011) 2497–2504. doi:10.1016/j.chroma.2011.02.056.

[25] C.M.M. Bougeard, E.H. Goslan, B. Jefferson, S.A. Parsons, Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine, Water Res. 44 (2010) 729–740. doi:10.1016/j.watres.2009.10.008.

[26] A.D. Nikolaou, T.D. Lekkas, M.N. Kostopoulou, S.K. Golfinopoulos, Investigation of the behaviour of haloketones in water samples, Chemosphere. 44 (2001) 907–912. doi:10.1016/S0045-6535(00)00536-1.

[27] S.K. Golfinopoulos, A.D. Nikolaou, Survey of disinfection by-products in drinking water in Athens, Greece, Desalination. 176 (2005) 13–24. doi:10.1016/j.desal.2004.10.029.

[28] X. Xu, T.M. Mariano, J.D. Laskin, C.P. Weisel, Percutaneous absorption of trihalomethanes, haloacetic acids, and haloketones, Toxicol. Appl. Pharmacol. 184 (2002) 19–26. doi:10.1016/S0041-008X(02)99494-9.

[29] J.W. Munch, United States Environmental Protection Agency, EPA Method 504.1, 1995, Cincinnati, OH. 1,2-Dibromoethane (EDB), 1,2-Dibromo-3-chloro-propane (dbcp), and 1,2,3-trichloropropane (123tcp) in water by microextraction and gas chromatography. https://www.epa.gov/quality/12-dibromoethane-edb-and-12-dibromo-3-chloropropane-dbcp-water-microextraction-and-gas (accessed 17 February 2020)

[30] S.K. Golfinopoulos, A.D. Nikolaou, The screening of disinfection by-products in large and small water systems in Greece, Desalin. Water Treat. 58 (2017) 80–85.

doi:10.5004/dwt.2017.0352.

[31] Y. Liu, J. Duan, W. Li, Q. Lai, C.P. Saint, D. Mulcahy, Determination of Volatile Disinfection Byproducts in Water by Gas Chromatography–Triple Quadrupole Mass Spectrometry, Anal. Lett. 48 (2015) 188–203. doi:10.1080/00032719.2014.930873.

[32] M. Serrano, M. Silva, M. Gallego, Fast and “green” method for the analytical monitoring of haloketones in treated water, J. Chromatogr. A. 1358 (2014) 232–239. doi:10.1016/j.chroma.2014.06.103.

[33] C. Martínez, V. Gómez, F. Borrull, E. Pocurull, Determination of Disinfection By-products in Water Samples from Advanced Membrane Treatments by Headspace Solid Phase Microextraction and, Anal. Bioanal. Chem. Res. 1 (2014) 38–49.

[34] M. Serrano, M. Silva, M. Gallego, Determination of 14 haloketones in treated water using solid-phase microextraction and gas chromatography-mass spectrometry, J. Chromatogr. A. 1407 (2015) 208–215. doi:10.1016/j.chroma.2015.06.060.

[35] J. Laaks, M.A. Jochmann, T.C. Schmidt, Solvent-free microextraction techniques in gas chromatography, Anal. Bioanal. Chem. 402 (2012) 565–571. doi:10.1007/s00216-011-5511-4.

[36] S. Pedersen-Bjergaard, K.E. Rasmussen, T. Grønhaug Halvorsen, Liquid-liquid extraction procedures for sample enrichment in capillary zone electrophoresis, J. Chromatogr. A. 902 (2000) 91–105. doi:10.1016/S0021-9673(00)00738-X.

[37] J. Lee, H.K. Lee, K.E. Rasmussen, S. Pedersen-Bjergaard, Environmental and bioanalytical applications of hollow fiber membrane liquid-phase microextraction: A review, Anal. Chim. Acta. 624 (2008) 253–268. doi:10.1016/j.aca.2008.06.050.

[38] A. Esrafili, M. Baharfar, M. Tajik, Y. Yamini, M. Ghambarian, Two-phase hollow fiber liquid-phase microextraction, TrAC - Trends Anal. Chem. 108 (2018) 314–322. doi:10.1016/j.trac.2018.09.015.

[39] J.M. Pearce, Building research equipment with free, open-source hardware, Science (80-.). 337 (2012) 1303–1304. doi:10.1126/science.1228183.

[40] S. Rosenberger, C. Laabs, B. Lesjean, R. Gnirss, G. Amy, M. Jekel, J.C. Schrotter, Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment, Water Res. 40 (2006) 710–720. doi:10.1016/j.watres.2005.11.028.

[41] B.M. Tymrak, M. Kreiger, J.M. Pearce, Mechanical properties of components fabricated with open-source 3-D printers under realistic environmental conditions, Mater. Des. 58 (2014) 242–246. doi:10.1016/j.matdes.2014.02.038.

[42] G. Lasarte-Aragonés, R. Lucena, S. Cárdenas, M. Valcárcel, Effervescence-assisted dispersive micro-solid phase extraction, J. Chromatogr. A. 1218 (2011) 9128–9134. doi:10.1016/j.chroma.2011.10.042.

[43] C.H. Chang, P.L. Urban, Fizzy Extraction of Volatile and Semivolatile Compounds into the Gas Phase, Anal. Chem. 88 (2016) 8735–8740. doi:10.1021/acs.analchem.6b02074.

[44] M.C. Dodd, N.D. Vu, A. Ammann, V.C. Le, R. Kissner, H.V. Pham, T.H. Cao, M. Berg, U. Von Gunten, Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: Relevance to drinking water treatment, Environ. Sci. Technol. 40 (2006) 3285–3292. doi:10.1021/es0524999.

[45] E. Carasek, J. Merib, Membrane-based microextraction techniques in analytical chemistry: A review, Anal. Chim. Acta. 880 (2015) 8–25. doi:10.1016/j.aca.2015.02.049.

[46] M. Ghambarian, Y. Yamini, A. Esrafili, Developments in hollow fiber based liquid-phase microextraction: Principles and applications, Microchim. Acta. 177 (2012) 271–294. doi:10.1007/s00604-012-0773-x.

[47] J. Zhang, H.K. Lee, Application of dynamic liquid-phase microextraction and injection port derivatization combined with gas chromatography-mass spectrometry to the determination of acidic pharmaceutically active compounds in water samples, J. Chromatogr. A. 1216 (2009) 7527–7532. doi:10.1016/j.chroma.2009.03.051.

[48] J. PłotkaWasylka, K. Owczarek, J. Namieśnik, Modern solutions in the field of microextraction using liquid as a medium of extraction, TrAC - Trends Anal. Chem. 85 (2016) 46–64. doi:10.1016/j.trac.2016.08.010.

[49] F. Peña, S. Cárdenas, M. Gallego, M. Valcárcel, Combining headspace gas chromatography with mass spectrometry detection for confirmation of hydrocarbon residues in virgin olive oil following automatic screening, J. Chromatogr. A. 1052 (2004) 137–143. doi:10.1016/j.chroma.2004.08.020.

[50] I. Montesinos, M. Gallego, Headspace gas chromatography-mass spectrometry for rapid determination of halonitromethanes in tap and swimming pool water, in: Anal. Bioanal. Chem., 2012: pp. 2315–2323. doi:10.1007/s00216-011-5516-z.

[51] X. Liu, Z. Shen, P. Wang, C. Liu, Z. Zhou, D. Liu, Effervescence assisted on-site liquid phase microextraction for the determination of five triazine herbicides in water, J. Chromatogr. A. 1371 (2014) 58–64. doi:10.1016/j.chroma.2014.10.068.

[52] M. Yang, X. Wu, Y. Jia, X. Xi, X. Yang, R. Lu, S. Zhang, H. Gao, W. Zhou, Use of magnetic effervescent tablet-assisted ionic liquid dispersive liquid-liquid microextraction to extract fungicides from environmental waters with the aid of experimental design methodology, Anal. Chim. Acta. 906 (2016) 118–127. doi:10.1016/j.aca.2015.12.019.

[53] R.S. Zhao, W.J. Lao, X.B. Xu, Headspace liquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination, Talanta. 62 (2004) 751–756. doi:10.1016/j.talanta.2003.09.035.

[54] N. Vora-adisak, P. Varanusupakul, A simple supported liquid hollow fiber membrane microextraction for sample preparation of trihalomethanes in water samples, J. Chromatogr. A. 1121 (2006) 236–241. doi:10.1016/j.chroma.2006.04.009.

[55] C. Worawit, W. Alahmad, M. Miró, P. Varanusupakul, Combining graphite with hollow-fiber liquid-phase microextraction for improving the extraction efficiency of relatively polar organic compounds, Talanta. 215 (2020). doi:10.1016/j.talanta.2020.120902.

[56] I. Montesinos, M. Gallego, Speciation of common volatile halogenated disinfection by-products in tap water under different oxidising agents, J. Chromatogr. A. 1310 (2013) 113–120. doi:10.1016/j.chroma.2013.08.036.

[57] J. On, H. Pyo, S.W. Myung, Effective and sensitive determination of eleven disinfection byproducts in drinking water by DLLME and GC–MS, Sci. Total Environ. 639 (2018) 208–216. doi:10.1016/j.scitotenv.2018.05.077.

[58] H. Ma, Y. Li, H. Zhang, S.M. Shah, J. Chen, Salt-assisted dispersive liquid-liquid microextraction coupled with programmed temperature vaporization gas chromatography-mass spectrometry for the determination of haloacetonitriles in drinking water, J. Chromatogr. A. 1358 (2014) 14–19. doi:10.1016/j.chroma.2014.06.021.

[59] A. Domínguez-Tello, A. Arias-Borrego, T. García-Barrera, J.L. Gómez-Ariza, Seasonal and spatial evolution of trihalomethanes in a drinking water distribution system according to the treatment process, Environ. Monit. Assess. 187 (2015). doi:10.1007/s10661-015-4885-8.

[60] A. Domínguez-Tello, A. Arias-Borrego, T. García-Barrera, J.L. Gómez-Ariza, A two-stage predictive model to simultaneous control of trihalomethanes in water treatment plants and distribution systems: adaptability to treatment processes, Environ. Sci. Pollut. Res. 24 (2017) 22631–22648. doi:10.1007/s11356-017-9629-6.

Table 1. Figures of merit of the extraction method (EA-SHF-LPME/GC-ECD and GC-MS).

Analyte	m/z	Linear Range (µg L^{-1})	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})	E_e	Repeatability (n=5) Inter-day (%RSD)		Reproducibility (n=10) Intra-day (%RSD)		Recovery (n=5) %		E_e (M1)
							0.5 µg L^{-1}	10 µg L^{-1}	0.5 µg L^{-1}	10 µg L^{-1}	0.5 µg L^{-1}	10 µg L^{-1}	
TCM	47, **83**, 85	0.117-50	0.980	0.035	0.117	16.3	7	5	8	7	89	89	25.7
BDCM	**83**, 85, 129	0.033-50	0.991	0.010	0.033	29.1	10	8	10	8	91	90	35.7
DBCM	79, 127, **129**	0.050-50	0.997	0.015	0.050	34.7	9	9	10	9	103	100	29.3
TBM	171, **173,** 175	0.067-50	0.995	0.020	0.067	39.1	5	4	5	5	98	97	30.7
BNM	46, **93**, 95	0.731-20	0.999	0.22	0.731	13.1	8	7	8	7	79	84	30.2
TCNM	46, **117**, 119	0.040-60	0.995	0.012	0.040	29.6	8	6	8	7	92	93	37.8
DBNM	46, 171, **173**	0.073-30	0.999	0.022	0.073	27.7	11	10	10	10	98	99	16.4
BCNM	46, 127, **129**	0.086-30	0.998	0.026	0.086	31.8	6	5	6	5	95	95	22.1
CNM	46, **49**, 51	0.403-30	0.999	0.145	0.403	47.7	13	13	12	11	84	85	10.7
DCNM	46, **83**, 85	0.190-30	0.999	0.058	0.190	45.4	5	5	6	7	93	95	19.5
CAN	40, 48, **75**	0.258-30	0.998	0.079	0.258	59.5	12	11	12	11	97	99	4.9
BAN	40, **119**, 121	0.150-20	0.998	0.045	0.150	58.2	3	3	5	4	92	96	9.5
BCAN	**74**, 76, 155	0.140-40	0.998	0.042	0.140	54.5	11	10	11	9	95	96	11.3
DBAN	**118**, 120, 199	0.056-60	0.998	0.017	0.056	32.1	12	11	13	12	99	99	31.6
DCAN	74, 82, 84	0.060-40	0.998	0.018	0.060	92.0	6	5	6	6	103	100	19.7
TCAN	73, **108**, 110	0.057-40	0.999	0.017	0.057	16.7	15	13	16	15	97	97	19.6
1,3-DCA	49, **77**, 79	0.033-20	0.998	0.010	0.033	71.1	10	9	10	8	88	87	5.8
1,1,1-TCA	**43**, 125, 127	0.053-40	0.998	0.016	0.053	140.1	6	6	6	6	113	100	4.4

Ee = enrichment factor = concentration of analyte in the acceptor phase (c_a) divided by the initial concentration in the sample (c_d); Ee = c_a/c_d,
Ee (M1) = enrichment factor in the method without effervescence
m/z ions: mass to change ratio of the specific fragments used for the selected ion monitoring MS analysis

Table 2. Results of the analyses (n = 3) of water samples by the proposed method EA-SHF LPME GC-µECD/MS.

	DS (1) Aljaraque		DS (2) Lepe		DS (3) Tinto			DS (4) Riotinto			DS (5) La Palma		DS (6) Andévalo	
	Alj WTP (1)	RSB (1)	Lep WTP (2)	RAY(.2)	Tin WTP (3)	MOG (3)	BEA (3)	Rti WTP (4)	RZL (4)	FLC (4)	Lpa WTP (5)	RBL (5)	And WTP (6)	RTH (6)
pH	7.11	7.37	7.11	7.15	7.44	7.43	7.28	7.14	7.29	8.39	6.85	6.9	7.17	7.01
T ºC	20.5	21.9	20.8	20.6	20.4	22.2	23.3	20.4	21	23.3	20.2	19.9	18.8	19.3
Cond	290	301	296	284	271	299	306	152	166	200	328	302	294	306
DOC	2.99	1.88	1.66	2.02	2.11	2.31	3.28	2.88	2.72	3.11	1.89	2.54	1.32	2.149
UV $_{254}$	0.0301	0.0253	0.0234	0.0292	0.0301	0.0386	0.0376	0.0297	0.0310	0.034	0.0211	0.0275	0.0101	0.0218
DBPs														
TCM	15.9 ± 2.1	9.4 ± 1.6	13.4 ± 1.3	21.0 ± 2.0	22.1± 3.2	26.8 ± 1.6	27.2 ± 2.3	21.4 ± 1.8	34.6 ± 2.4	45.0 ± 3.1	5.1 ± 0.2	44.3 ± 3.4	5.9 ± 0.3	5.8± 1.1
BDCM	16.4 ± 1.2	8.3± 0.6	12.7± 0.4	18.3 ± 1.4	14.6 ± 0.8	20.4 ± 1.9	23.6 ± 2.2	18.6 ± 0.7	14.8 ± 3.3	14.2 ± 1.9	8.2 ± 0.6	16.1 ± 1.1	4.3± 0.2	6.3 ± 0.3
DBCM	11.2 ± 0.4	5.4 ± 0.2	11 ± 0.3	10.4 ± 0.4	16.2 ± 0.9	13.2 ± 1.1	15.1 ± 1.6	10.9 ± 0.4	3.8 ± 0.1	4.3 ± 0.2	7.6 ± 0.8	14.4± 1.1	3.2± 0.9	10.1 ±0.8
TBM	2.1 ± 0.2	3.7 ± 0.1	4.8 ± 0.5	3.14 ± 0.6	1.0 ± 0.3	2.9 ± 0.4	1.9 ± 0.1	4.3 ± 0.2	2.4 ± 0.1	3.9 ± 0.4	3.21 ± 0.1	4.0± 0.1	2.5± 0.1	2.9 ± 0.5
BNM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.03 ± 0.4	n.d.	0.49 ± 0.2	3.43 ± 0.6	3.37 ± 0.3	0.61 ± 0.2	n.d.
BCAN	0.51 ± 0.2	0.19 ± 0.1	2.63 ± 0.4	2.07 ± 0.5	0.45 ± 0.2	1.53 ± 0.5	0.54 ± 0.2	0.92 ± 0.3	1.00 ± 0.3	0.27 ± 0.1	0.17 ± 0.2	n.d.	n.d.	n.d.
DBAN	n.d.	2.13 ± 0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DCAN	0.33 ± 0.1	0.13 ± 0.1	1.29 ± 0.3	0.79 ± 0.2	0.38 ± 0.1	0.61 ± 0.2	0.31 ± 0.1	0.54 ± 0.2	0.58 ± 0.2	0.18 ± 0.1	n.d.	0.23 ± 0.1	n.d.	n.d.
1,3DCA	n.d.	n.d.	n.d.	n.d.	1.02 ± 0.3	n.d.	0.98	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Average of concentration found (µg L^{-1})

n.d: not detected

Figure captions

Figure 1. Sampling points and characteristics of the water distribution systems.

Figure 2. Modular supporting device for the SHF-LPME extraction designed by a 3D printer.

Figure 3. Comparison between the Spiral- and U-shaped HF-LPMEs.

Figure 4. Effects of: A) the extraction temperature (ºC), B) extraction time, C) selection of sample pH, and D) the addition of salt (sodium sulfate) and an organic modifier (MTBE).

Figure 5. Effect of effervescence on the extraction of 18 DBPs at different molar ratios.

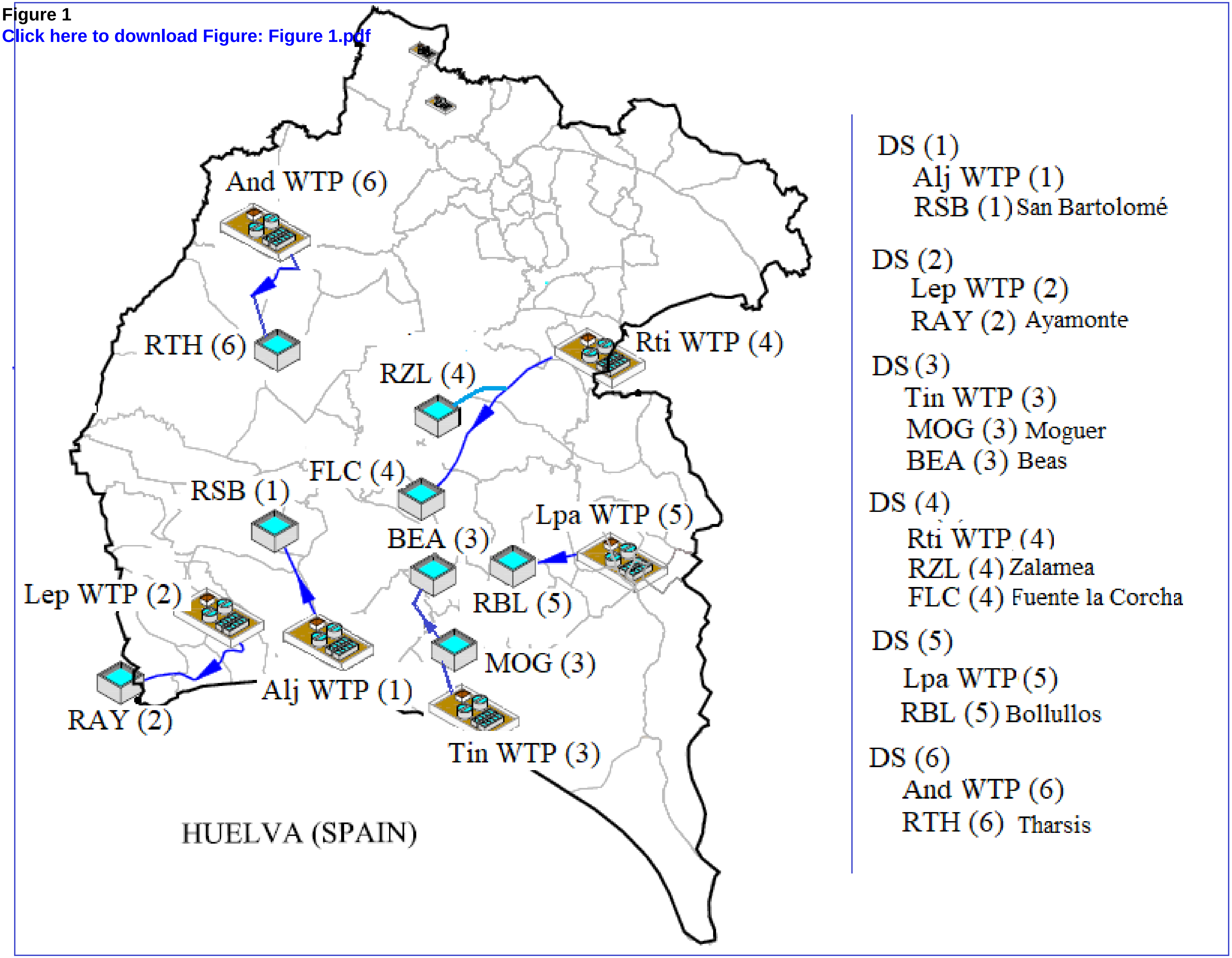
Figure 6. GC-µECD chromatogram obtained from a standard solution at 10 µg L^{-1}, using A) SHF LPME and B) EA-SHF LPME.

Tables

Table 1. Figures of merit of the extraction method (EA-SHF-LPME/GC-ECD and GC-MS).

Table 2. Results of the analyses (n = 3) of water samples by the proposed method EA-SHF LPME GC-µECD/MS.

Figure 1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RTH (6)
RZL (4)
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FLC (4)
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BEA (3)
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RBL (5)
Lep WTP (2)
MOG (3)
RAY (2)
Alj WTP (1)
Tin WTP (3)
HUELVA (SPAIN)
DS (1)
Alj WTP (1)
RSB (1) San Bartolomé
DS (2)
Lep WTP (2)
RAY (2) Ayamonte
DS (3)
Tin WTP (3)
MOG (3) Moguer
BEA (3) Beas
DS (4)
Rti WTP (4)
RZL (4) Zalamea
FLC (4) Fuente la Corcha
DS (5)
Lpa WTP (5)
RBL (5) Bollullos
DS (6)
And WTP (6)
RTH (6) Tharsis

Figure 2

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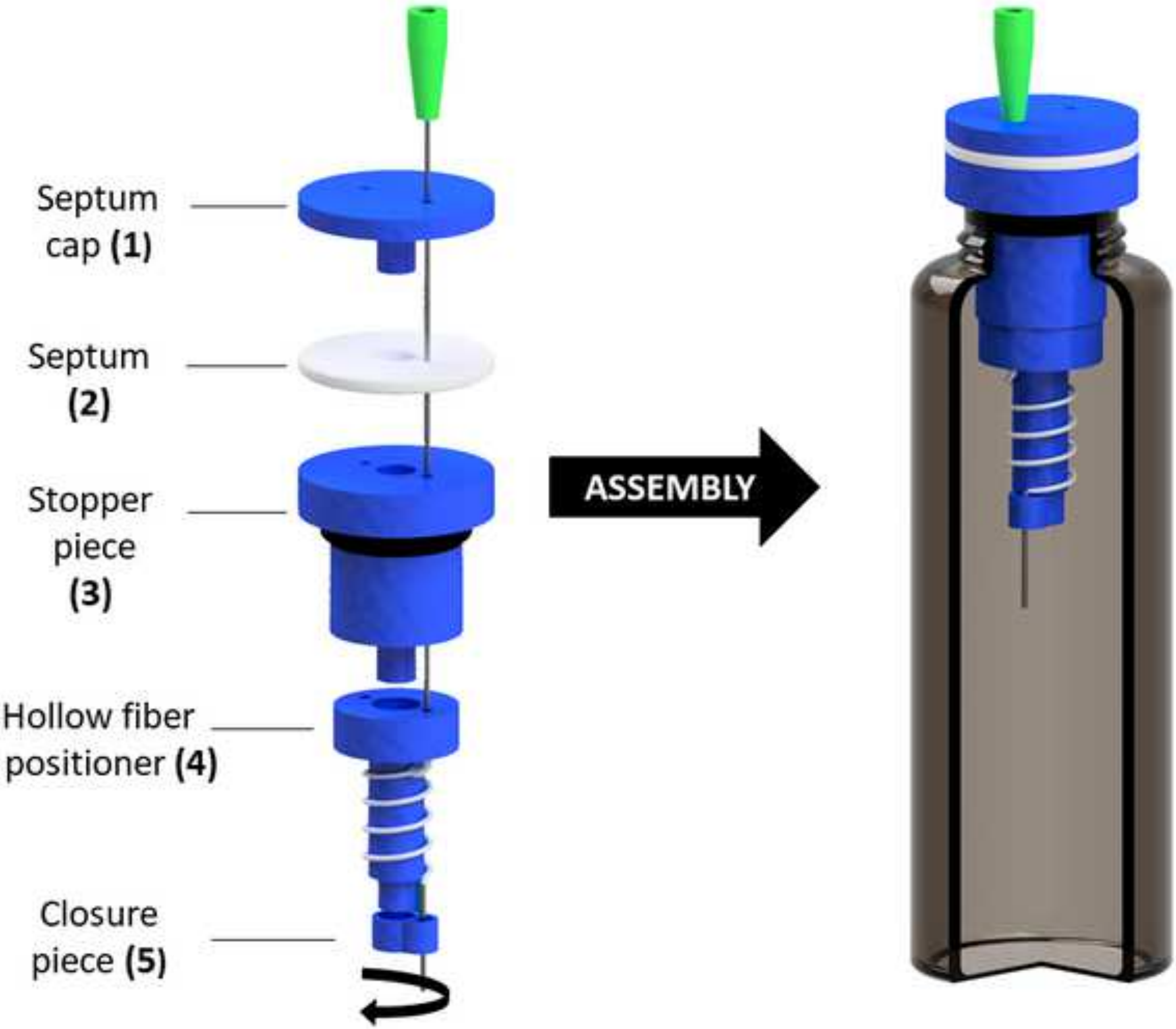
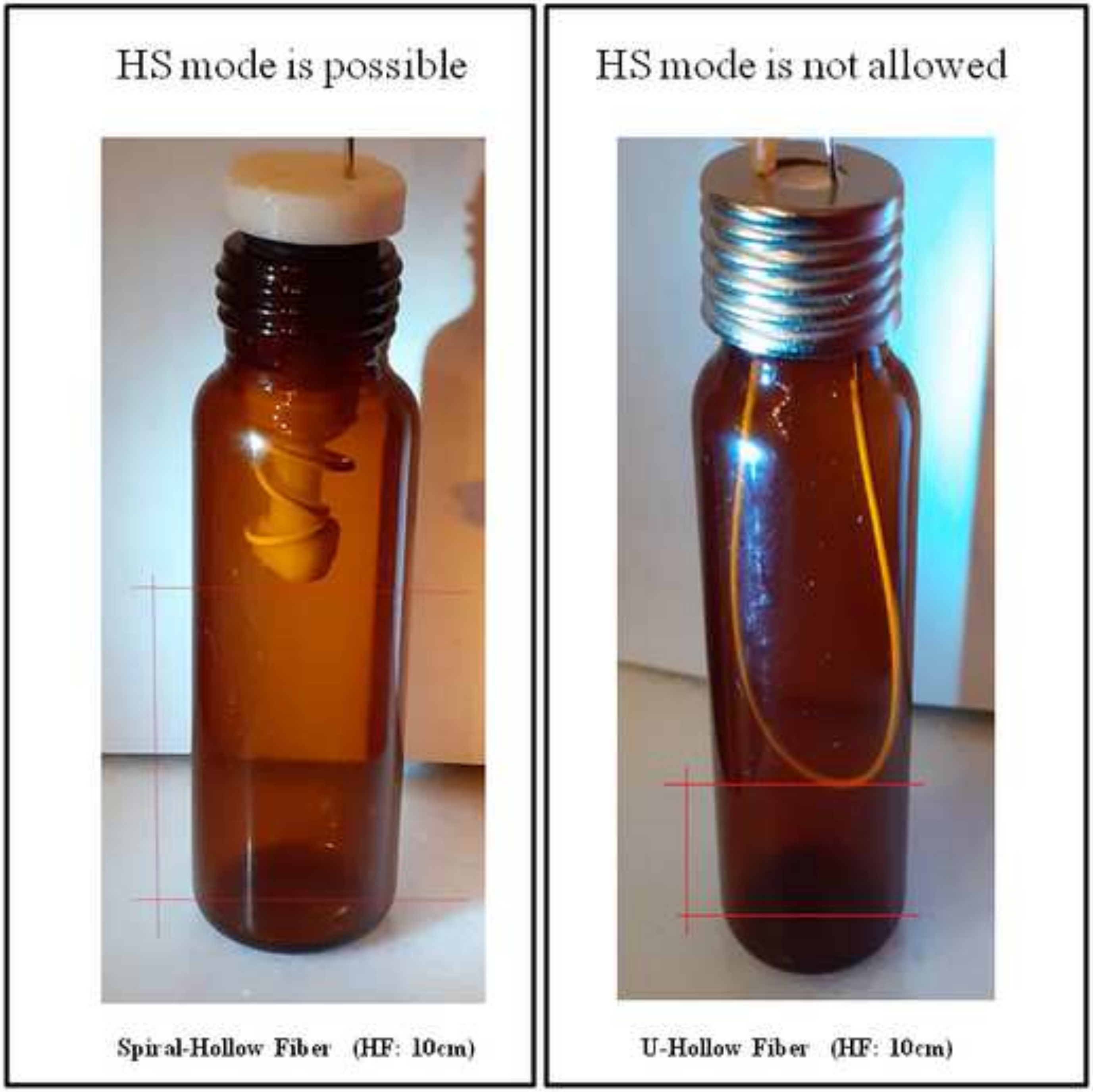


Figure 3



HS mode is possible

Spiral-Hollow Fiber (HF: 10cm)

HS mode is not allowed

U-Hollow Fiber (HF: 10cm)

Figure 4

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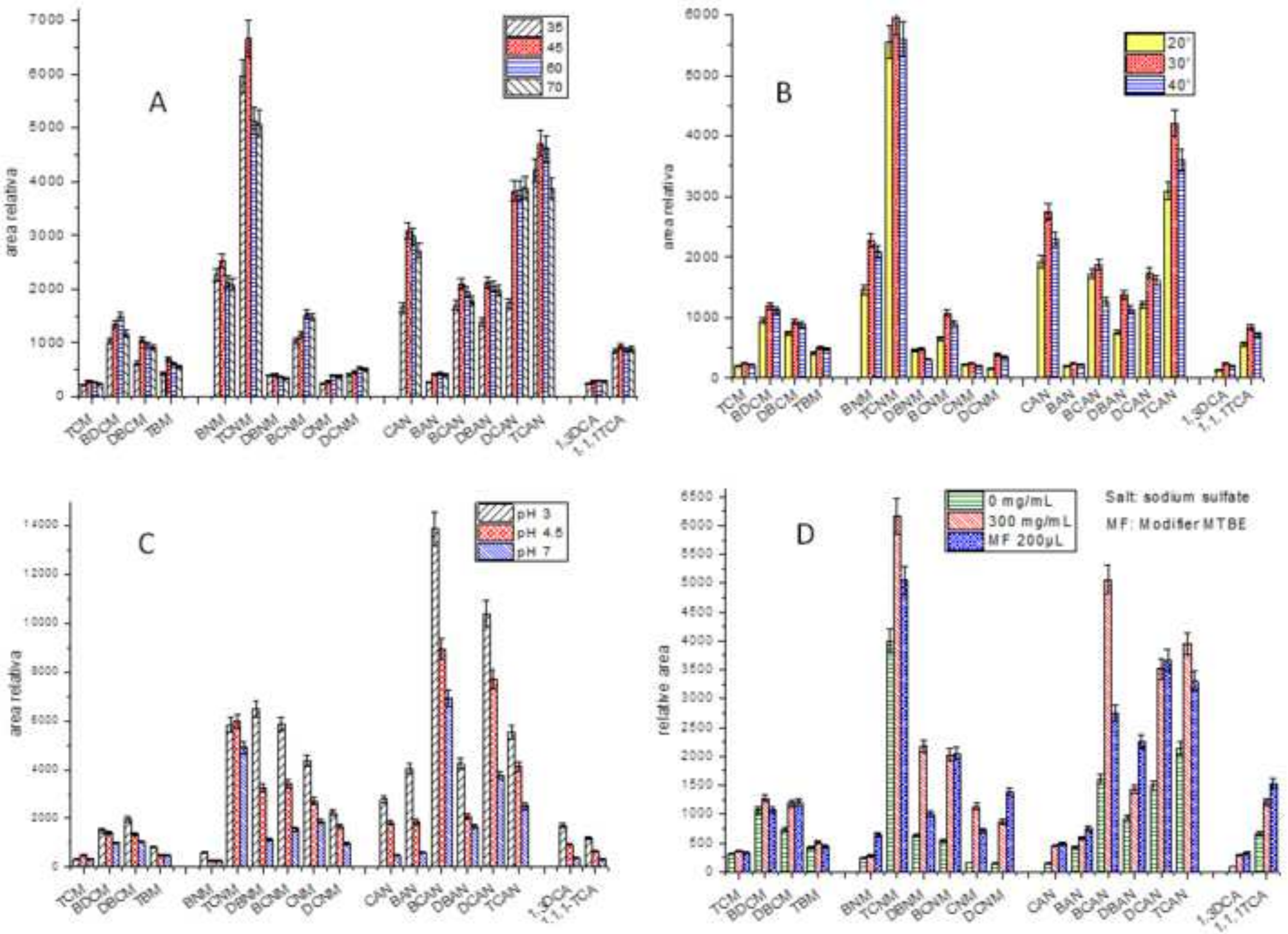

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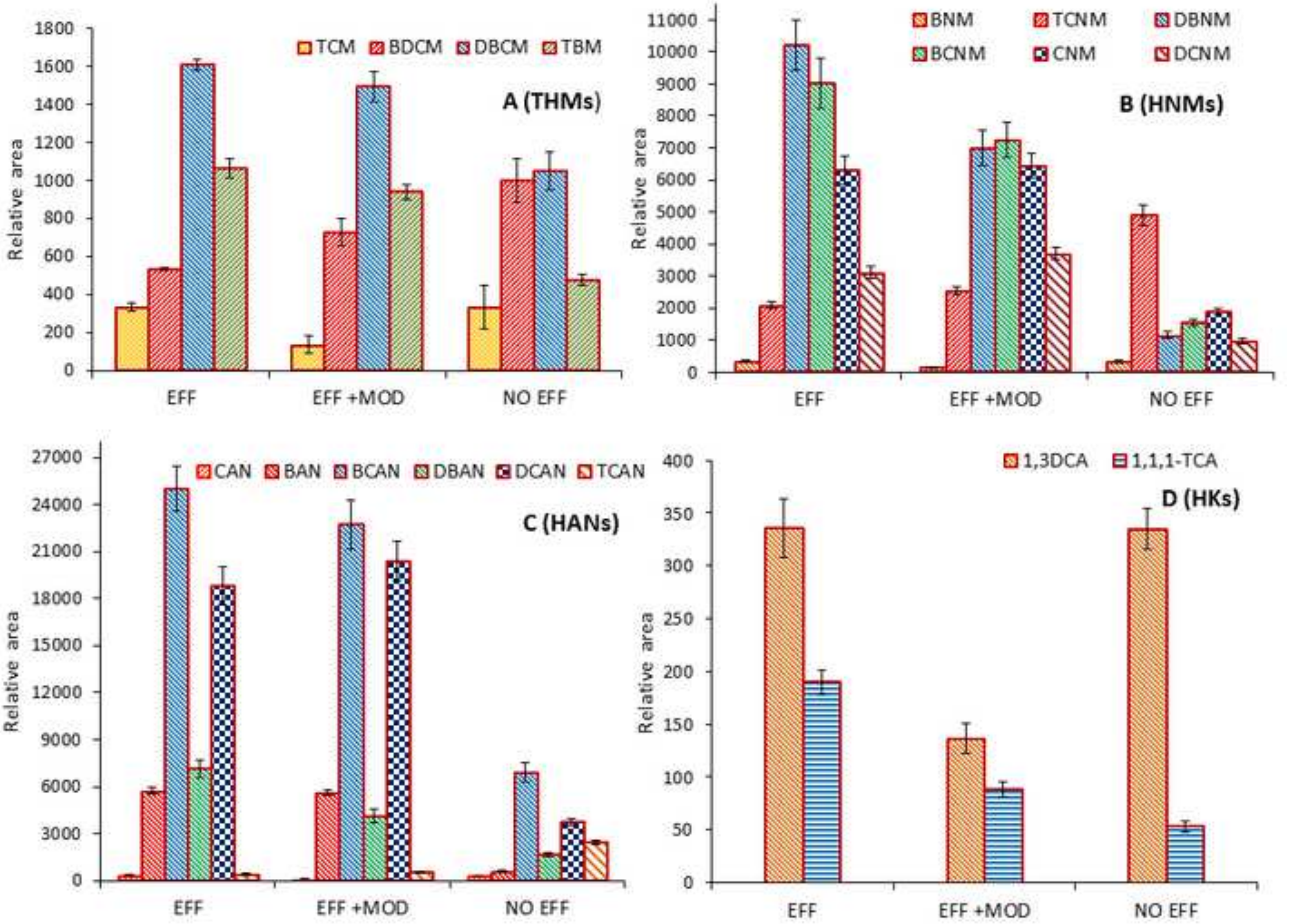
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CNM
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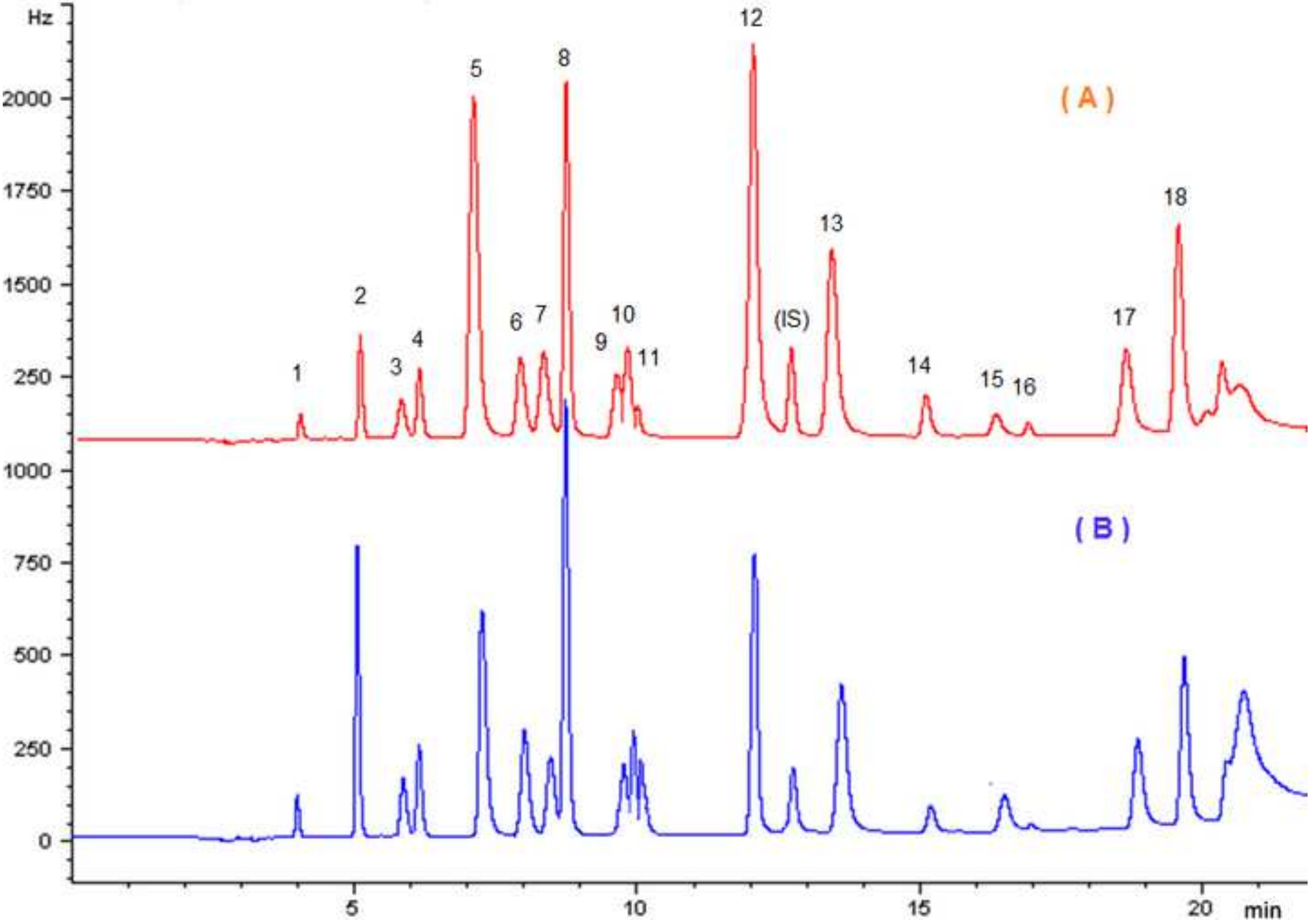
Figure 6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***Credit Author Statement**

ADT: Conceptualization, Methodology, Investigation, Validation, Writing-original draft, Resources; ADA: Investigation; JLGA: Funding acquisition, Resources, Investigation; AAB: Supervision, Methodology, Investigation, Validation, Writing-review and editing; TGB: Supervision, Conceptualization, Methodology, Investigation, Writing-original draft, Writing-review and editing, Funding acquisition, Resources.

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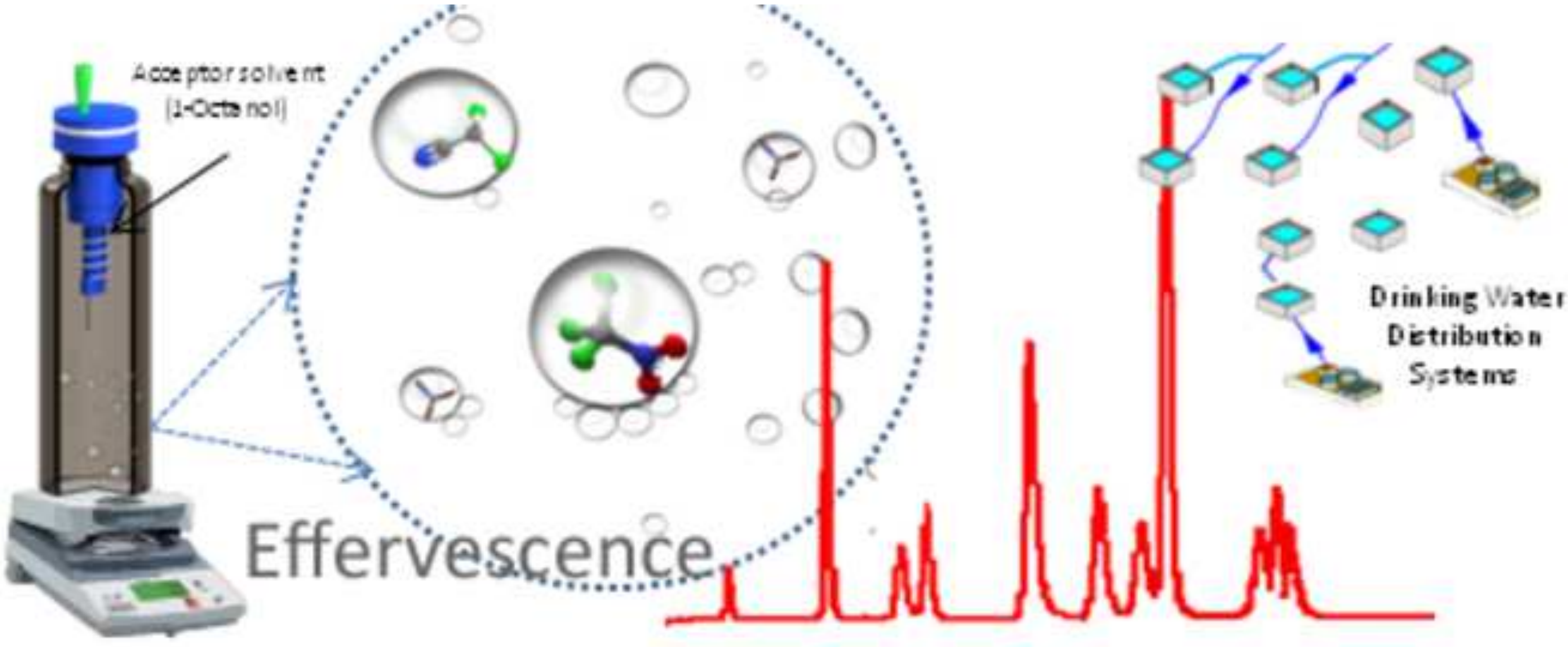
Graphical Abstract



Highlights

- Microextraction of 18 DPBs with spiral hollow fiber (SHF) in HS
- Modular extraction support device was performed using a 3D printer
- Support device allowed long length of fiber and reduce errors source
- The effervescence effect improves the extraction efficiency
- BNM, BCAN, DBAN DCAN and 1,3 DCA were detected in supply water