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Dispersive liquid–liquid microextraction with non-halogenated extractants for trihalomethanes determination in tap and swimming pool water

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ABSTRACT

An effective, low solvent consumption, reduced cost and high throughput sample preparation method for the determination of four trihalomethanes (THMs) in tap and swimming pool water samples is presented. THMs extraction and concentration were performed by dispersive liquid–liquid microextraction (DLLME), based on the use of non-halogenated and low volatile solvents as extractants. Analytes were further determined by gas chromatography with micro-electron capture detection (GC-microECD). Under optimized conditions, the proposed method uses 18 mL volume samples, 0.7 mL of acetone (dispersant) and 0.05 mL of 1-undecanol (extractant). Achieved enrichment factors (EFs) varied from 67 to 104 times, the limits of quantification (LOQs) stayed between 0.05 and 1.3 ng mL^{-1}, and an excellent linearity was noticed up to 100 ng mL^{-1}. Relative recoveries, measured for spiked aliquots of tap and swimming pool water samples, remained between 79% and 113%, with associated standard deviations below 12%. The applicability of the developed methodology was demonstrated with chlorinated water samples analysis. As regards tap water samples, the sum of THMs concentrations remained under the limit fixed by the European Union (100 ng mL^{-1}); however, some samples contained levels close to 80 ng mL^{-1}, the maximum allowable concentration established by the United States Environmental Protection Agency (EPA).

1. Introduction

Water is one of the main transmitting agents of pathogen microorganisms; therefore, it is necessary to perform disinfection steps during the drinkable making process. Among chemical disinfectants employed in treatment plants, free chlorine ($HClO/ClO^-$) remains as one of the most effectives in terms of cost and efficiency. Moreover, its high stability ensures also the microbiological quality of water through the supplying net [1]. On the other hand, free chlorine reacts with organic matter present in water rendering the so-called disinfection by-products (DBPs) [2]. Most DBPs are halogenated species generated in a different extent depending on variables such as the amount and type of organic matter, pH, temperature, free chlorine dose, presence of halide salts (particularly bromide) and organic nitrogen. Overall, trihalomethanes (THMs) are the most abundant DBPs, and also the most concerning ones due to their negative impact on human health, including a positive correlation between THMs exposure and the incidence of certain cancers [3].

In order to prevent such effects, different organisms have established the maximum allowable concentrations of THMs in drinking water. Particularly, the United States Environmental Protection Agency (EPA) and the European Union (EU) have set these limits at 80 and 100 ng mL^{-1}; respectively, refereed to the sum of trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM) [4].

THMs are usually determined by gas chromatography (GC), with electron capture detection (ECD), or in combination with mass spectrometry (GC–MS) [5]. As regards the sample preparation step, different methodologies have been proposed aiming (1) to provide limits of quantification (LOQs) far below legal thresholds, (2) to obtain accurate data, and (3) to achieve low cost and organic solvent consumption, as well as high throughput, analytical procedures. The most resorted techniques are conventional liquid–liquid extraction (LLE) [6–8], headspace (HS) methodologies [9], purge and trap (P&T) [10–13] and solid-phase microextraction (SPME) [14–18]. Solvent consumption requirements of LLE are overcome by HS, P&T and SPME. However, the on-line combination of HS and P&T devices with the GC system requires a considerable investment and, depending on the considered design, the risk of cross-contamination problems, due to THMs residues remaining in different elements of the system is not negligible.

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In addition to above approaches, several liquid-phase microextraction (LPME) modalities, such as single drop microextraction (SDME) [19,20] and hollow fiber (HF)-LPME [21], have been also proposed for THMs extraction and concentration from water samples. SDME and HF-LPME employ very low volumes of organic solvents and show also a low cost; however, similar to SPME, they display relatively slow extraction kinetics. This problem is overcome by the dispersive liquid–liquid microextraction (DLLME) technique, introduced by Rezaee et al. [22]. In DLLME, a binary solvent solution consisting of a water immiscible extractant, with a different water density, and a dispersant miscible with both, extractant and water, is added to the sample. Dispersion of fine extractant droplets in the aqueous phase leads to fast extraction kinetics and high yields. Despite the number of successful DLLME applications developed during last 5 years [23,24], only one work has addressed the determination of THMs using carbon disulfide(CS_2) as extractant [25]. Likely, high toxicity of the most common extractants used in DLLME (carbon tetrachloride, chlorobenzene, trichloroethane, etc.), blank problems due to the presence of TCM traces in these extractants and difficulties to separate the chromatographic peak of the solvent from those corresponding to target analytes are responsible for the scarce interest in evaluating DLLME for the monitoring of THMs in chlorinated water samples.

The aim of this study was to assess the possibility of developing a new DLLME-based method, to be used in combination with GC-microECD, suitable for THMs determination in tap and swimming-pool water samples, avoiding the use of high toxic solvents, minimizing contamination problems and/or peaks overlapping risks, and maintaining the typical features of DLLME, such as high enrichment factors, fast kinetics, accuracy and low cost. In order to conquer these goals, non-chlorinated solvents displaying (1) much lower volatility than target analytes and (2) negligible ECD responses were considered as extractants.

2. Experimental section

2.1. Standards, solvents and material

Chromatographic analysis grade 1-undecanol (99%) and hexadecane (99%), 1,2-dibromopropane (97%), employed as internal surrogate (I.S.) in the sample preparation process, and a solution of the four THMs (TCM, BDCM, DBCM, and TBM) in methanol (200 μg mL^{-1} each) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Methanol and acetonitrile, HPLC-grade, and acetone, trace analysis, were acquired from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system (Millipore, Billerica, MA, USA). The stock solution of THMs was diluted with methanol and used to spike samples employed during optimization of DLLME conditions. Methanol was also used to prepare the stock and the diluted solutions of the I.S. GC-microECD determination conditions were optimized with THMs standards, containing a fixed amount of I.S., dissolved in both solvents considered as extractants (1-undecanol and hexadecane) in the DLLME step. All standard solutions were stored in the dark, at 4 °C.

2.2. Samples and sample preparation

Tap and swimming pool water samples were collected in glass flasks, without head space volume, and stored at 4 °C, for a maximum of 24 h before analysis. For optimization experiments, ultrapure water aliquots spiked at the 30 ng mL^{-1} level were used. Under final working conditions, extractions were performed in 20 mL volume glass tubes, furnished with a PTFE covered septum and aluminum caps, containing 0.9 g of NaCl and 18 mL of water. The binary extraction mixture, consisting of 0.70 mL of acetone and 0.05 mL of 1-undecanol, was injected in the tube through the septum with a glass syringe. Afterwards, samples were manually shaken (1 min) and centrifuged for 10 min at 3000 rpm. Extraction tubes were cooled down in the fridge (15 min) and the solidified floating drop of 1-undecanol was removed with a spatula and transferred to a 0.2 mL insert in a 1.5 mL autosampler vial. The extract was allowed to melt at room temperature, and injected (1 μL) in the GC-microECD system.

2.3. Equipment

An Agilent (Wilmington, DE, USA) 6890 model gas chromatograph (GC) equipped with a micro-electron capture detector (microECD) was used for analytes determination. The system was furnished with autosampler, split/splitless injector and electronic pressure control. Analytes were separated either with an Agilent HP-1 type capillary column (30 m × 0.25 mm i.d., df: 1 μm), operated at a constant helium flow of 1 mL min^{-1}, or with a SPB-1 type megabore column (30 m × 0.53 mm i.d., df: 5 μm), provided by Supelco (Bellefonte, PA, USA), operated at a constant helium flow of 5 mL min^{-1}. Unless otherwise stated, reported data correspond to the megabore column. With the capillary HP-1 column, the oven was initially held at 45 °C for 1 min and then raised to 110 °C at 5 °C min^{-1}, to 260 °C at 20 °C min^{-1} and held at 260 °C for 3 min. With the megabore column the temperature program was as follows: 1 min at 50 °C, 1st ramp at 5 °C min^{-1} to 160 °C (held for 1 min), 2nd ramp at 25 °C min^{-1} to 260 °C (held for 5 min). Injections in the megabore column were made in the splitless mode, with the solenoid valve switching to the split position after 0.2 min (split flow 50 mL min^{-1}). On the other hand, the split mode (split flow 10 mL min^{-1}) was used with the capillary column in order to prevent peak broadening. In both cases, injector and detector were set at 260 °C and 300 °C, respectively. Nitrogen was used as make-up gas in the microECD at a constant flow of 40 mL min^{-1}.

2.4. Quantification

The effects of different parameters in the efficiency of the DLLME process were assessed using, either the peak area measured for each compound as response variable, or considering the enrichment factors (EFs) achieved under investigated conditions. EFs are defined as the ratio between THMs concentrations in DLLME extracts and those added to water samples. The first values were established by comparison with calibration curves obtained for standards prepared in 1-undecanol. The absolute extraction efficiencies (EEs, %) of the optimized method were evaluated with the following equation: $EEs = EFs \times V_e \times 100/V_s$; being V_e and V_s the volumes of recovered organic extract (0.045 mL) and water sample (18 mL), respectively.

Quantification of THMs levels in tap and swimming pool water samples was carried out by pseudo-external calibration, employing the curves built with ultrapure water aliquots, containing a fixed level of the I.S. (20 ng mL^{-1}) and increasing concentrations of THMs between their LOQs and 100 ng mL^{-1} per compound. Aqueous calibration standards were submitted to the whole DLLME process and added concentrations plotted against the ratio of analyte/I.S. peak area.

3. Results and discussion

3.1. Optimization of DLLME conditions

3.1.1. Extractant and dispersant selection

In DLLME, the characteristics of the extractant exert a major effect in the efficiency of the microextraction process. Selected

solvents must fulfill several requirements, such as high affinity for target species, low water solubility, possibility to be easily recovered from the extraction vessel, compatibility with the GC technique and do not interfere the chromatographic peaks of target analytes [23,24]. Obviously, a low toxicity is also advisable. Several of the above requirements make difficult the applicability of DLLME to THMs determination, since many high density, chlorinated extractants, easily recovered from the bottom of the extraction tube after phase separation, interfere the chromatographic peaks of volatile THMs and saturate the response of the ECD detector; furthermore, they might contain impurities of TCM. Thus, carbon disulfide (CS_2), a high toxic solvent, remains as the only option of volatile, high density extractant for DLLME of THMs [25]. As an alternative, the feasibility of using non-halogenated solvents, displaying lower than water densities, as extractants in the DLLME of THMs was assessed. We select 1-undecanol and hexadecane since (1) their high melting points (11–16 °C) allowed to freeze the organic phase [26], floating above the water sample in the extraction tube after the centrifugation step, facilitating its separation from the liquid sample in comparison with toluene, 1-hexanol and 1-octanol also employed in DLLME [23,24]; furthermore, (2) they do not overlap the chromatographic peaks of target analytes with any of both GC columns considered in this research. The repeatability of the injection for THMs standards in 1-undecanol and hexadecane remained below 6.5%, an excellent linearity (R^2 values above 0.9990) was observed up to 2000 ng mL^{-1} and the instrumental limits of quantification (LOQs), defined for a signal to noise of 10, ranged from 1 to 4 ng mL^{-1}.

Fig. 1 compares the responses obtained for DLLME of spiked ultrapure water samples (10 mL aliquots) with 1-undecanol and hexadecane. In both cases, acetone was employed as dispersant. Extractant and dispersant volumes were set at 0.1 and 0.5 mL, respectively. As noticed, the higher peak areas, for all compounds, corresponded to 1-undecanol, the most polar solvent, which was chosen for further series of experiments.

In DLLME, formation of the cloudy stage is crucial for a fast and effective extraction process. Water soluble, polar solvents (e.g. methanol, acetone, acetonitrile) are normally used to disperse the droplets of extractant in the aqueous sample [22–24]; moreover, sonication has been also proposed as an effective mode to achieve an emulsion between the sample and the water-insoluble extractant. This variation of the DLLME technique is usually reported as USAEME (ultrasound-assisted emulsification-microextraction) [24,27]. Its major advantages are (1) further reduction in the consumption of organic solvents and (2) higher extraction efficiencies than conventional DLLME, since avoiding the use of dispersant reduces the solubility of the analytes in the water

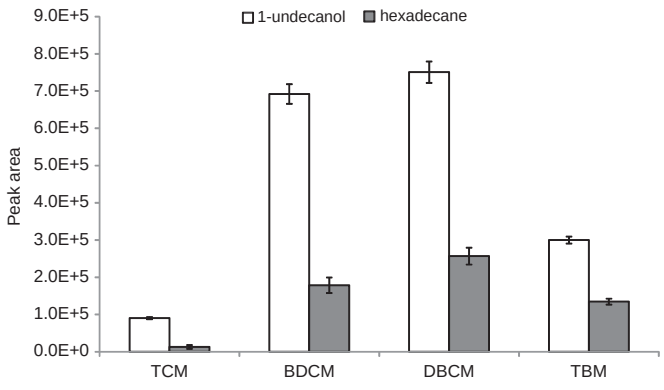

Fig. 1. Comparison of responses for 1-undecanol and hexadecane used as extractant solvents, $n=3$ replicates.

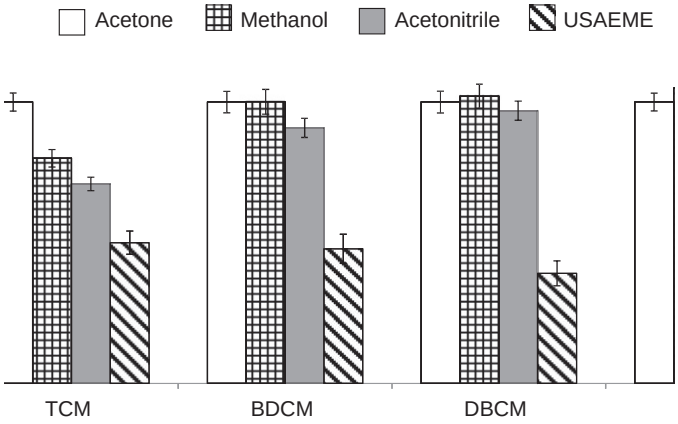

Fig. 2. Normalized responses for different dispersants, including the comparison of DLLME with USAEME, using 1-undecanol (0.1 mL) as extractant, $n=3$ replicates.

sample. Fig. 2 shows the normalized responses obtained for three different dispersants (0.5 mL each) and also by USAEME, soaking the spiked water samples (10 mL aliquots) for 10 min in an ultrasound bath. In all cases, 1-undecanol (0.1 mL) was considered as extractant. As observed, the lower responses for the four THMs corresponded to the replacement of the organic dispersant by ultrasound energy (USAEME methodology), which points out to a less effective emulsification in the latter situation. Acetone provided higher responses than methanol and acetonitrile for TCM, whereas very little, or non significant, variations were noticed for the rest of THMs. On the basis of these data, considering also its lower toxicity, acetone was kept as dispersant.

3.1.2. Ionic strength

Salt addition produces several effects in the efficiency of DLLME. On one hand, it increases slightly the organic phase volume due to a diminution in the solubility of the extraction solvent (1-undecanol) in the aqueous sample. This fact origins more diluted extracts. On the other hand, the salting out effect improves the extraction efficiency of polar, non-ionic species using any non-exhaustive microextraction technique [24]. Finally, salt addition might worsen the extraction kinetics due to an increase in the viscosity of the sample, slowing down the transference of the analytes from the sample to the dispersed droplets of 1-undecanol. Experimentally, the effect of the ionic strength was evaluated with samples (10 mL) containing increasing percentages of NaCl (0%, 2%, 5%, 10% and 20%). Obtained results showed an increase in the responses of target compounds up to 5% of NaCl, remaining constant at higher levels (Fig. 3). The positive effect of salt addition was most significant for TCM and BDCM, the most polar THMs involved in this study. In agreement with this finding, most SPME studies have reported a positive influence of salt addition on the yield of the extraction [15,18]; however, in the previous application of DLLME to THMs extraction, considering CS_2 as extractant, the effect of the ionic strength in the extraction yield was reported as negligible [25].

3.1.3. Sample, dispersant and extractant volumes

The influence of these three variables on the efficiency of the extraction process was evaluated simultaneously with a factorial experimental design, considering each variable at two levels. Their low and high level values were 10–18 mL for sample volume (code A), 0.5–1 mL dispersant volume (code B) and 0.05–0.1 mL extractant volume (code C). Such values were selected on the basis of the capacity of extraction vessels (20 mL), previous applications of the DLLME technique [22–24]

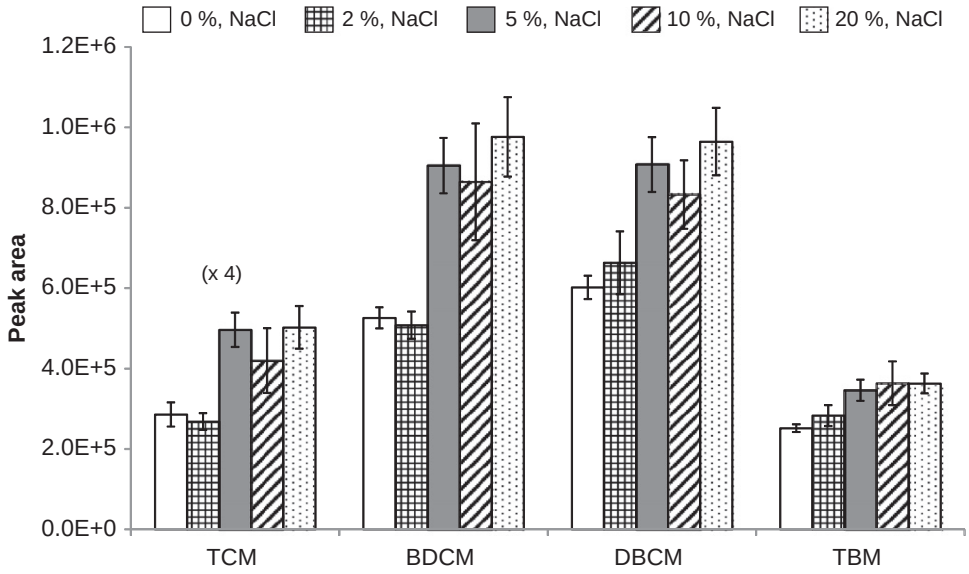

Fig. 3. Effect of NaCl addition in the efficiency of the DLLME method, $n=3$ replicates.

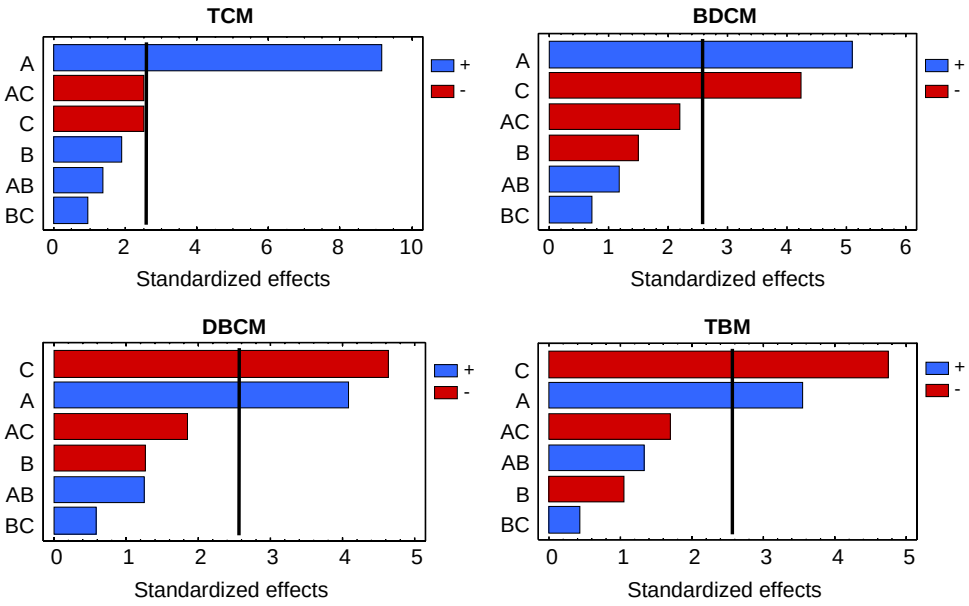

Fig. 4. Standardized Pareto charts for TCM, BDCM, DBCM and TBM as function of sample (A), dispersant (B) and extractant (C) volumes.

and the requisite of obtaining a volume of extract high enough to be handled with the autosampler of the GC-microECD system. In the central point of the design, the DLLME process was repeated ($n=4$) to evaluate the extraction error. In all experiments, 1-undecanol and acetone were employed as extractant and dispersant, respectively; moreover, samples contained a 5% (w/v) of NaCl. EF values, which are directly related with the LOQs of the overall method, were used as response variable. Obtained values (see Supplementary information, Table S1) were analyzed using the Statgraphics software (Manugistics, Rockville, MD, USA) in order to assess the main effects and two-factor interactions in the achieved EFs.

Fig. 4 graphically summarizes the standardized values of main effects and two-factor interactions. The length of depicted bars is proportional to the variation of EFs when the considered factor changes from the low to the high level, within the domain of the design. A positive sign indicates an improvement in the EFs and, a negative one, the opposite trend. The vertical line represents the limit of statistical significance, defined for a 95% confidence level. The volume of sample (code A) played a positive and statistically significant influence on the EFs of all compounds, being the most important variable for TCM and BDCM. On the other hand, increasing the volume of extractant (code C) exerted a negative effect, being statistically significant except for TCM. Finally, neither the volume of acetone (code B), nor two-factor interactions showed statistically significant effects. Taking into account these comments, sample and 1-undecanol volumes were set at 18 and 0.05 mL, respectively; whereas, an intermediate value (0.7 mL) was further used as acetone volume. Under these conditions, the recovered volume of 1-undecanol extract was 0.045 ± 0.001 mL.

3.1.4. *Extraction and centrifugation times*

Both variables were evaluated to maximize the response of the analytes. In DLLME, the extraction time is defined as the interval

comprised between injection in the sample of the mixture of extractant and dispersant, and the beginning of centrifugation. During this time, tubes were manually shaken to keep the emulsion. Values of 1, 5, and 10 min were considered. This variable did not show any influence on the analytes extraction (data not given). Thus, 1 min was set as the extraction time.

The centrifugation time was investigated in 5, 10, and 15 min. The use of a 5 min centrifugation step gave lower responses for all compounds, probably due to an incomplete separation of the 1-undecanol phase, whereas no differences were observed between 10 and 15 min. Therefore, 10 min was selected as the working value for centrifugation time.

3.2. Performance of the analytical methodology

Under final optimized conditions, the DLLME method provided EFs comprised between 67 and 104 times, (Table 1). Considering 18 mL volume samples and 0.045 mL as the volume of the solidified 1-undecanol phase (measured with a micro-syringe after melting at room temperature), above EFs corresponded to absolute extraction efficiencies (EEs, %) from 16% to 26%, in the same order of values as those reported by Kozani et al. [25] (from 15% to 45%) using CS_2 as extractant.

The linearity of the method was investigated with ultrapure and tap water samples. In the first case, aliquots spiked at eight different concentrations, from 1 to 100 ng mL^{-1}, were used, whereas, seven addition levels (5–100 ng mL^{-1}) were considered for tap water. In both cases, the I.S. was added at 20 ng mL^{-1}. Ratios between THMs and I.S. peak areas were plotted versus added concentrations and fitted to a linear model. Determination coefficients (R^2) above 0.993 were obtained for both samples; moreover, ratios between slopes for calibration curves of ultrapure and tap water remained between 1.01 and 1.09, suggesting a very limited influence of the matrix on the efficiency of the extraction (Table 2).

Procedural blanks, corresponding to ultrapure water, showed the existence of a small signal at the retention time of TCM, which was confirmed using the capillary column; thus, its LOQ was calculated as the standard deviation corresponding to this peak for six procedural blanks, multiplied by 10 and divided by the addition curve slope. A LOQ of 1.3 ng mL^{-1} was obtained for TCM (Table 2). The rest of THMs were not detected in procedural blanks; therefore, their LOQs were estimated from the signal to noise ratios (S/N) corresponding to their chromatographic peaks in ultrapure water aliquots spiked with 1 ng mL^{-1} of these species. In this case, LOQs varied between 0.05 and 0.1 ng mL^{-1} (Table 2). Globally, LOQs compiled in Table 2 are similar to those reported for methodologies such as P&T (0.06–2.1 ng mL^{-1}) [14], HS SPME with PDMS–DVB (0.09–0.72 ng mL^{-1}) [18] and PDMS (3–6 ng mL^{-1}) coated fibers [16], HF-LPME (0.03–0.6 ng mL^{-1}) [21], SDME (0.5–1.2 ng mL^{-1}) [19] and DLLME with CS_2 as extractant (0.03–0.6 ng mL^{-1}) [25]. On the other hand, LOQs in the low ng per liter range can be achieved with P&T systems furnished with a capillary trap, cooled down with liquid nitrogen [13], and HS extraction followed by analytes concentration in a solid sorbent packed into the programmable temperature vaporization (PTV) injector of the GC system [9]. Obviously, these two latter approaches require the use of dedicated and relatively expensive instrumentation.

Precision was assessed with samples spiked at different concentration levels and processed under repeatability (intra-day precision) and reproducibility (inter-day precision) conditions. In the first case, the relative standard deviations (RSDs, %) of analytes responses (peak area/I.S. peak area) ranged from 1.0% to 15.5%, depending on the compound and the addition level (Table 3). Under reproducibility conditions, RSDs stayed between 9.2% and 13.1%, for samples spiked at 10 ng mL^{-1} per compound.

Given that similar slopes were attained for ultrapure and tap water samples (Table 2), it was investigated whether pseudo-external calibration, considering spiked aliquots of ultrapure water, could provide accurate data for tap and swimming pool water samples, or if the time-consuming standard addition methodology must be considered. To this end, differences between responses (analyte/I.S. peak area) measured for spiked and non-spiked aliquots of the above samples were quantified with calibration curves obtained for ultrapure water and found concentrations were compared with the added ones. Table 4 summarizes the relative recoveries obtained for tap and swimming pool water samples using both GC columns described in the experimental section. Obtained values varied from 79% to 113%, with standard deviations (SD) below 12% (Table 4), which confirms the suitability of pseudo-external calibration to quantify the levels of THMs in tap and swimming pool water.

Table 1
Average enrichment factors (EFs) and extraction efficiencies (EEs, %) rendered by the optimized DLLME method, $n=5$ replicates.

Compound	EFs	EEs (%)
TCM	67 ± 8	16 ± 2
BDCM	68 ± 4	17 ± 1
DBCM	87 ± 8	22 ± 2
TBM	104 ± 4	26 ± 1

Table 3
Relative standard deviations (RSDs, %) of the method for spiked samples.

Compound	Intra-day precision ($n=3$ replicates)			Inter-day precision ($n=12$ replicates, 3 days)
	[a]5 ng mL^{-1}	[a]40 ng mL^{-1}	[a]80 ng mL^{-1}	[a]10 ng mL^{-1}
TCM	15.5	11.0	5.2	9.2
BDCM	10.9	8.7	1.9	12.0
DBCM	8.2	7.8	1.0	12.7
TBM	6.0	7.3	4.0	13.1

[a] Added concentration.

Table 2
Linearity and limits of quantification (LOQs) of the optimized method.

Compound	Ultrapure water (1–100 ng mL^{-1})		Tap water (5–100 ng mL^{-1})		Ultrapure/tap water slopes ratio	LOQs (ng mL^{-1})
	Slope ± SD	R^2	Slope ± SD	R^2		
TCM	0.0070 ± 0.0004	0.998	0.0064 ± 0.0004	0.993	1.09	1.3
BDCM	0.061 ± 0.003	0.998	0.059 ± 0.001	0.994	1.03	0.05
DBCM	0.060 ± 0.002	0.998	0.059 ± 0.001	0.996	1.01	0.05
TBM	0.025 ± 0.001	0.998	0.024 ± 0.001	0.998	1.05	0.1

Table 4
Relative recoveries (%) for spiked water samples, $n=3$ replicates.

Compound	Recovery (%) ± SD					
	Tap water				Swimming pool water	
	[a]5 ng mL^{-1}		[a]30 ng mL^{-1}		[a]70 ng mL^{-1}	
	Column A	Column B	Column A	Column B	Column A	Column B
TCM	100 ± 3	108 ± 2	93 ± 7	83 ± 12	93 ± 3	97 ± 6
BDCM	99 ± 3	95 ± 3	88 ± 4	79 ± 7	92 ± 4	90 ± 5
DBCM	106 ± 1	107 ± 7	91 ± 5	90 ± 4	91 ± 2	93 ± 3
TBM	98 ± 1	96 ± 4	101 ± 4	113 ± 10	92 ± 1	87 ± 6

Column A, megabore column.
Column B, capillary column.
[a] Added concentration.

Table 5
Concentrations of THMs measured in water samples, $n=3$ replicates.

Code	Water type	Measured values (ng mL^{-1}) (SD)				Total THMs concentration (ng mL^{-1})
		TCM	BDCM	DBCM	TBM	
1	Tap	26 (4)	10 (1)	4.0 (0.4)	5 (1)	45
1[a]	Tap	22 (4)	10 (1)	5.0 (0.2)	6.5 (0.7)	44
2	Tap	63 (14)	14 (2)	2.0 (0.2)	0.5 (0.1)	80
3	Tap	27 (1)	10.0 (0.5)	2.0 (0.1)	n. d.	39
4	Tap	6 (1)	n. d.	n. d.	n. d.	6
4[a]	Tap	7 (1)	n.d.	n.d.	n.d.	7
5	Tap	42 (5)	7 (1)	1.0 (0.1)	n. d.	50
6	Tap	56 (4)	7.0 (0.4)	1.00 (0.03)	n. d.	64
7	Tap	46 (5)	7 (1)	1.00 (0.03)	n. d.	54
8	Tap	33 (1)	4.0 (0.1)	1.00 (0.02)	n. d.	38
9	Swimming pool	16 (2)	1.0 (0.1)	2.0 (0.1)	4.0 (0.5)	23
10	Indoor swimming pool	239 (33)[b]	1.0 (0.1)	1.0 (0.1)	1.0 (0.1)	242
11	Swimming pool	55 (3)	9.0 (0.7)	2.0 (0.3)	n.d.	66
12	Swimming pool	5.0 (0.4)	1.0 (0.1)	0.40 (0.03)	n.d.	7
13	Swimming pool	25 (2)	0.4 (0.1)	n.d	n.d.	26
13[a]	Swimming pool	25.0 (0.1)	0.5 (0.1)	0.20 (0.01)	n.d.	26

[a] Data obtained with the capillary column.
[b] Sample diluted five times for quantification.

3.3. Application to real samples

Table 5 summarizes the concentrations of THMs measured in different chlorinated water samples. Tap water specimens (codes 1–8) were obtained in different cities and villages from Galicia (Northwest Spain) between June 2011 and July 2011. TCM was quantified in all samples, with maximum values above 60 ng mL^{-1}. On the other hand, TBM was the compound displaying the lowest detection frequency with maximum values below 7 ng mL^{-1}. Although the sum of THMs concentrations in tap waters did not surpass the limit established by the EU (100 ng mL^{-1}), sample code 2 showed an overall THMs content of 80 ng mL^{-1}, equal to the maximum limit set by the EPA. Globally, THMs values measured in tap water remain in the same range of values as those reported for samples collected in other areas from Spain [14,18].

Samples from outdoor swimming pools (codes 9, and 11–13) did not present higher THMs concentrations than tap water. Although the organic load, and the levels of free chlorine, in swimming pools are higher than in tap water, the high volatility of THMs prevents their accumulation in this aquatic environment. On the other hand, the sample from the indoor swimming pool (code 10), showed a TCM content above 200 ng mL^{-1}. Although relatively high, this value stays within the range of concentrations (from 18 to 520 ng mL^{-1}) recently reported for TCM in indoor swimming pools [4].

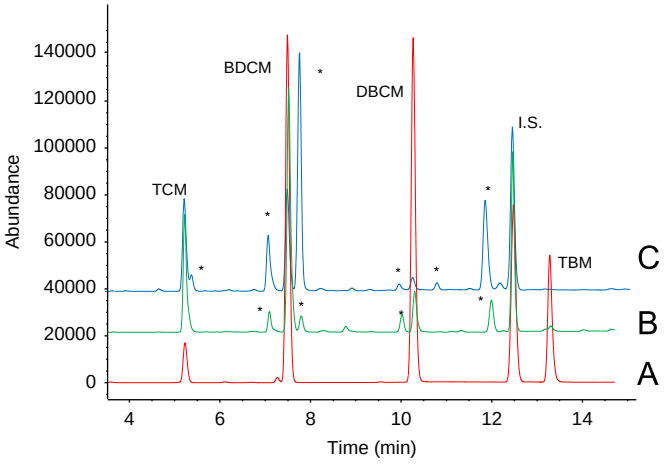

Fig. 5. Chromatograms corresponding to spiked (30 ng mL^{-1}) ultrapure water (A); tap water, code 2, Table 5 (B); and swimming pool water, code 11, Table 5 (C). * Non-identified compounds.

Fig. 5 shows the chromatograms corresponding to spiked (30 ng mL^{-1}) ultrapure water (A); tap water (code 2, Table 5) (B); and swimming pool water (code 11, Table 5) (C). In addition to THMs peaks, extra signals were observed in the GC-micro ECD chromatograms of real samples. In order to ensure that target

analytes responses are not overestimated due to co-elution with interferences, some samples (codes 1, 4 and 13) were also processed with the capillary column. As compiled in Table 5, an excellent agreement was observed between pairs of concentration values obtained with any of both columns.

4. Conclusions

The suitability of low toxicity and room-temperature melting point organic solvents for DLLME of THMs in tap and swimming pool water samples has been demonstrated for first time. Main advantages of the proposed approach are the rapid kinetics of the extraction process, the low cost of the sample preparation step, the reduced consumption of organic solvents and, consequently, the minimum generation of wastes. Furthermore, the method renders an excellent accuracy, acceptable precision, low LOQs and a linear response interval up to the maximum allowable concentration of THMs in tap water. Although, the DLLME step itself is hardly automated, the methodology reported in this work provides enough extract volume to be further handled with a conventional autosampler, which improves sample throughput versus manual injection considered in most DLLME applications. Thus, the optimized method might be a valuable alternative to the use of more expensive sample preparation techniques, such as HS, P&T and SPME, for those laboratories processing a limited number of sample specimens, which cannot afford a full-time dedicated GC system for THMs determinations.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.07.041.

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