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Sensitive determination of 2,4,6-trichloroanisole in water samples by ultrasound assisted emulsification microextraction prior to gas chromatography–tandem mass spectrometry analysis

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ABSTRACT

A novel application of an ultrasound assisted emulsification microextraction (USAEME) technique is proposed for the extraction and preconcentration of 2,4,6-trichloroanisole (2,4,6-TCA) from water samples prior to its determination by gas chromatography–tandem mass spectrometry (GC–MS/MS). USAEME employs a non-polar high-density solvent (extractant solvent), which forms an oil-in-water emulsion (O/W) in the aqueous sample bulk assisted by ultrasonic radiation. Several factors including, solvent type and volume, extraction time, extraction temperature, shaking mode and matrix modifiers were studied and optimized over the relative recovery of the target analyte. An aliquot of 5 mL water sample was conditioned by adding 150 μL 6.15 mol L^{-1} sodium chloride and 300 μL 0.05 mol L^{-1} phosphate buffer (pH 6), and finally extracted with 40 μL chloroform by using USAEME technique. Under the optimal experimental conditions 2,4,6-TCA was quantitatively extracted achieving an enrichment factor (EF) of 555. The detection limit (LOD), calculated as three times the signal-to-noise ratio (S/N), was 0.2 ng L^{-1} and the RSD was 6.3% ($n = 5$) when 1 ng L^{-1} 2,4,6-TCA standard mixture was analyzed. The coefficients of estimation of the calibration curves obtained following the proposed methodology was ≥0.997 and the linear working range was 1–5000 ng L^{-1}. Finally, the proposed technique was successfully applied for extraction and determination of the 2,4,6-TCA in water samples. Recovery studies lead values ≥94%, which showed a successfully robustness of the analytical methodology for determination of nanogram per liter of 2,4,6-TCA in water samples.

1. Introduction

Taste and odour of the surface water supplies and especially of the drinking water reservoirs is a key problem which produce the majority of complaints received by companies supplying drinking water. The descriptions of taste and odours most frequently cited by consumers are chlorine and earthy-musty odour [1]. The main compounds responsible for earthy-musty odours in drinking water are haloanisoles, geosmin and 2-methylisoborneol (MIB) [2,3]. Occurrence of MIB and geosmin in water has been associated with the presence of actinomycetes or their metabolic products, as well as with the presence of cyanobacteria and fungi [3,4]. Water chlorination results in the formation of several halogenated-disinfection by-products that may be responsible for poor water quality [5]. Some of them have been identified as natural halogenated products, others can be formed when active chlorine species react with dissolved organic matter [6,7]. 2,4,6-TCA is most probably formed by microbiological methylation of halophenols during water treatment or during transport through the distribution system [2,8]. 2,4,6-TCA is able to confer a musty taste and odour at low concentration, been its perception threshold lower than 4 ng L^{-1} [2]. Therefore, the identification and quantification of disinfection by-products in water samples has been an analytical challenge for years, because accurate determination at nanogram per liter is not straightforward. The analytical methodologies for determining these types of compounds require highly sensitive and selective analytical techniques for their unequivocal identification and determination. In this way, and considering the physicochemical properties of these semi-volatile compounds, gas chromatography coupled to mass spectrometry has been the choice for analysis of off-flavor compounds in water samples [9,10]. Different sample preparation strategies have been proposed, including closed-loop stripping (CLSA), liquid–liquid extraction (LLE), purge-and-trap, headspace solid-phase microextraction (HS-SPME) and stir bar sorptive extraction (SBSE) [10–17]. Recently, microextrac-

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tion techniques have gained interest in the analytical chemistry field. Miniaturization of LLE, reduction of organic solvents consumption and improvement of the extraction efficiency are some of the potential advantages of microextraction techniques. In this way, several different types of liquid-phase microextraction (LPME) have been developed including, single drop microextraction (SDME) [18], hollow fiber LPME [19], headspace LPME [20] and dynamic LPME [21]. Regueiro et al. [22] have introduced a novel modality of liquid–liquid microextraction, referred as ultrasound assisted emulsification microextraction (USAEME). USAEME employs a non-polar high-density solvent (extractant solvent), which form an oil-in-water emulsion (O/W) in the aqueous sample bulk assisted by ultrasound (US) waves. The application of US waves is an efficient tool to facilitate the emulsification phenomenon and this leads to a reduction of droplet size of the extractant phase. The droplet-size reduction leads to significant enlargement of the contact surface between both immiscible liquids improving the mass-transfer of the analyte between the two phases [23]. After centrifugation, the extractant phase settles at the bottom of the tube preconcentrating the analyte. An aliquot of the extractant phase is injected into the analytical instrument for analyte determination. USAEME is an efficient, simple, rapid and non-expensive alternative to other extraction techniques such as conventional LLE, SPME, SBSE and other LPME techniques. Furthermore, it is environmentally friendly because of the low organic solvent consumption. Up to now, USAEME has been successfully applied to the extraction and preconcentration of synthetic musk fragrances, phthalate esters, lindane, polybrominated diphenyl ethers, polychlorinated biphenyls and phenolic preservatives in aqueous samples [22,24–26].

In this work, we propose and demonstrate that USAEME technique can be successfully applied for extraction and preconcentration of "earthy-musty" odorous compounds from water samples and further determination by GC–MS/MS. To this end and considering that as far as off-flavor and odours of drinking water are due to disinfection by-product such as 2,4,6-TCA; this analyte was selected as representative compound for analytical studies. The influence of several variables on the performance of the technique were studied and optimized. The analytical performance of the proposed USAEME–GC–MS/MS was evaluated in terms of LODs, repeatability, linear working range and EF. The procedure was applied for determination of 2,4,6-TCA in drinking, lake and river water samples and its robustness was evaluated in terms of recovery factors (RF%).

2. Experimental

2.1. Reagents

The standard of 2,4,6-TCA (99%, solid crystal form) was purchased from Sigma–Aldrich (Steinheim, Germany). The internal standard (IS) 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) was purchased from Accustandard (New Haven, CT, USA). Stock solution of both were prepared in methanol at concentration of 1000 mg L^{-1} and stored in brown bottles at −20 °C. Working standard solutions were prepared daily in methanol and stored at 4 °C.

Methanol, chloroform and trichloroethene were purchased from Merck (Darmstadt, Germany) and carbon tetrachloride was purchased from Sigma–Aldrich. Sodium chloride, hydrochloric acid, sodium hydroxide and potassium phosphate were all purchased from Merck. Ultrapure water (18 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Paris, France). All reagents were of analytical grade or above.

2.2. Equipment and working conditions

A 40 kHz and 600 W US-bath with temperature control (Test Lab, Buenos Aires, Argentina) was used for assisting the emulsification process of the microextraction technique. The volume of extraction phase was measured using a 50 μL and 250 μL Hamilton syringe (Reno, NV, USA). Injections into the GC were made by using a 5 μL Hamilton syringe. GC–MS analyses were performed on a Varian 3900 gas chromatograph equipped with an ion trap mass detector Varian Saturn 2000 (Varian, Walnut Creek, CA, USA). The system was operated by Saturn GC–MS WorkStation v6.4.1 software. The GC column used was VF-5ms (25 m × 0.25 mm, 0.25 μm film thickness; Varian, Lake Forest, CA, USA). The temperature program was: 70 °C, held for 2 min; rating 20 °C min^{-1} to 150 °C; held for 1 min, rating 20 °C min^{-1} to a final temperature of 280 °C and held for 7 min. Helium (purity 99.999%) was used as a carrier gas a flow rate of 1.0 mL min^{-1}. The injector temperature was set at 280 °C and the injections were performed in the splitless mode. The mass spectrometer was operated in electron impact ionization mode at 70 eV. The trap, manifold and transfer line temperatures were 220 °C, 120 °C and 280 °C, respectively. Samples were analyzed in MS/MS mode. The peak identification was based on the relative retention time, base peak and isotopic pattern of the 2,4,6-TCA. Specific ions were selected from 2,4,6-TCA MS/MS spectra and the resulting base ion was the quantitative ion. Quantification of 2,4,6-TCA was carried out by using m/z 195 and 197 and m/z 324, 326, 328 were selected for IS. Relative retention time and peak quantification were performed against IS (BDE-47).

2.3. Sampling and sample preparation

For tap water samples collection, domestic water was allowed to run for 20 min and then collected. River water was collected from *Las Tunas River*, *Tupungato* District, and *Cipolleti Lake*, *Lujan de Cuyo* District, both from Mendoza Province. River and lake water samples were both collected at a depth of 20 cm. The total volume of each water sample was 1000 mL. All samples were collected free of air bubbles in amber glass containers and carried to the laboratory in cooled boxes. Once in the laboratory, samples were filtered through 0.22 μm pore size membrane filters and analyzed within 24 h.

2.4. USAEME procedure

A 5 mL aliquot of water sample was placed in a 10 mL glass-centrifuge tube, subsequently 150 μL 6.15 mol L^{-1} sodium chloride and 300 μL 0.05 mol L^{-1} phosphate buffer (pH 6) were added. Finally, 40 μL of chloroform was added and mixed up. The resulting mix was immersed into an ultrasonic bath for 5 min at 30 ± 2 °C. During sonication, the solution became turbid due to the dispersion of fine chloroform droplets into the aqueous bulk. The emulsion was centrifuged at 3500 rpm (1852.2 × g) for 2 min in order to disrupt the emulsion and separate the phases. After centrifugation, the extraction solvent remained at the bottom of the conical tube (ca. 9 μL). A 1 μL aliquot of the chloroform phase was removed from the bottom of the centrifuge tube and injected into gas chromatograph instrument.

3. Results and discussion

LPME efficiency for 2,4,6-TCA can be affected by several working parameters, including type and volume of extraction solvent, salting out effect, sample pH, extraction time and temperature as well as centrifugation time. The study and optimization of the above mentioned variables were performed by modifying one at a time while keeping the remaining constant. A 5 mL aqueous solution containing 1 μg L^{-1} of 2,4,6-TCA was used to perform the assays, which were done by triplicate. The chromatographic peak area was the parameter used to evaluate the influence of those variables on the relative recovery of USAEME technique.

3.1. Effect of extraction solvent

The extraction solvent is critical for developing an efficient USAEME technique since its physicochemical properties govern the emulsification phenomenon and the relative recovery of the technique. First of all, the analyte has to have high affinity for the extraction solvent. This solvent has to be water immiscible in order to form an efficient emulsion in aqueous sample and easily separated from the aqueous bulk. Additionally, it has to be compatible with the analytical instrumentation to be used. On the other hand, it was found convenient for practical purposes, that the extraction phase remain at the bottom of the centrifuge tube after phase separation; therefore it density should be higher than the water one. Taking into account these considerations three organic solvents, including carbon tetrachloride, chloroform and trichloroethene were examined. The density and water solubility values of the selected organic solvents are 1.58 g mL^{-1} and 0.8 mg mL^{-1} (carbon tetrachloride), 1.48 g mL^{-1} and 8 mg mL^{-1} (chloroform) and 1.46 g mL^{-1} and 1.2 mg mL^{-1} (trichloroethene).

The compatibility of these solvents with the USAEME technique was studied by adding 50 μL of each of the solvents mentioned above. The extraction procedure was the one described in Section 2.4. It was observed that the three studied solvents were able to form an emulsion during sonication leading to a biphasic system after centrifuging the solution. The results revealed that the relative recovery of chloroform was higher than trichloroethene and carbon tetrachloride one. The achieved results could be due to the emulsification efficiency of the solvents in the aqueous bulk due to the vapor pressure. The vapor pressures for the studied solvents are: chloroform, 21.2 kPa; trichloroethene, 7.7 kPa and carbon tetrachloride, 12.2 kPa. The induction of cavitation is difficult in a solvent of low vapor pressure because fewer vapors will enter the bubble. A more volatile solvent will support a higher cavitation at lower acoustic energy and produce vapor-filled bubbles [27]. When these bubbles are broken in a part, smaller droplets are formed favoring the emulsion formation and thus relative recovery of the technique. In this sense, chloroform was selected as the extraction solvent for further studies.

3.2. Effect of extraction solvent volume

The volume of extraction solvent to be added in order to obtain the highest extraction efficiency of the technique and the highest relative recovery of the analyte was studied within a volume range of 20–200 μL. The extraction procedure was the one described above. Volumes smaller than 35 μL were completely dissolved in the aqueous bulk. From Fig. 1 it is possible to observe that the greater relative recovery for 2,4,6-TCA was obtained when 40 μL chloroform was used to carry out USAEME. By increasing the volume of chloroform from 40 to 200 μL, the extraction phase volume increased and the relative recovery of the analyte decreased due to a dilution effect of it. Therefore; 40 μL chloroform was selected in order to obtain higher relative recovery and lower detection limit.

3.3. Effect of salting out and sample pH

Ionic strength can affect the affinity of the analytes for the extraction phase, the extraction solvent solubility and the aqueous bulk viscosity. All these aspects alter the emulsification phenomenon conditioning the mass-transfer process of the analyte from the sample bulk into the extraction phase micro-volume. Additionally, changes in the medium viscosity can affect the US-wave propagation. As the viscosity of the medium increase, the US-wave can be absorbed and dispersed as calorific energy; thus, the cavitation process is withdrawn and the organic phase cannot be dispersed in fine droplets [28]. Therefore, emulsion can

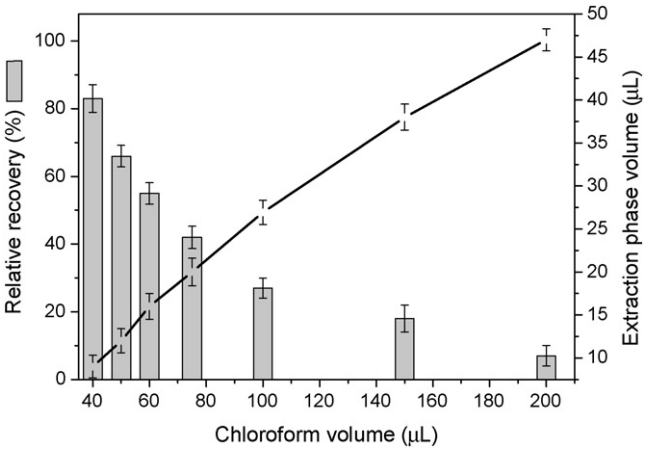

Fig. 1. Correlation between the added chloroform, extraction phase volume and relative recovery of 2,4,6-TCA. Extraction conditions: sample volume, 5 mL; extraction solvent, chloroform; extraction time, 5 min; centrifugation time, 2 min; extraction temperature, 20 °C. 2,4,6-TCA concentration: 1 μg L^{-1}.

be drastically minimized, diminishing thus, the efficiency of the mass-transfer process and consequently, the extraction efficiency of the technique [22]. Taking into in account all these considerations, the salting out study was carried out by adding different volumes of 6.15 mol L^{-1} sodium chloride to the extraction system. The assayed volumes were within the range; 0.00–2.8 mL. The extraction procedure was the one described in Section 2.4. Considering that chloroform solubility in water varies according to the salt concentration, the amount of needed organic solvent to collect the same volume of extraction solvent was determined experimentally. Thus, 4.4 μL chloroform by each 150 μL of salt was required in order to collect the same volume of extraction solvent phase. The results of salting out are showed in Fig. 2. The best relative recovery was observed in the volume range of 0.07–0.28 mL of 6.15 mol L^{-1} sodium chloride, with a maximum relative recovery for 0.15 mL. A slight increment of the sodium chloride volumes increases the ionic strength of the aqueous sample diminishing the affinity of 2,4,6-TCA for the aqueous bulk and enhancing the relative recovery of the extraction solvent. At high sodium chloride volumes the solubility of extraction solvent decreased, increasing the extraction phase volume and diminishing the relative recovery of the analyte due to a dilution effect of it. Therefore, 150 μL of 6.15 mol L^{-1} sodium chloride was chosen as working conditions for further studies.

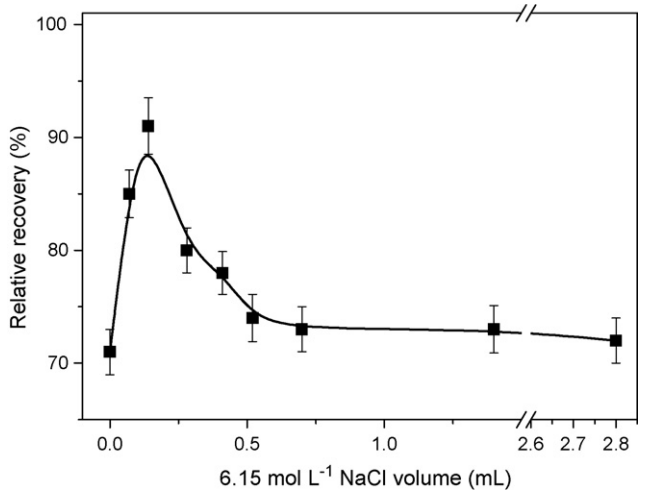

Fig. 2. Salting out effect on the relative recovery of 2,4,6-TCA. Extraction conditions as described in Fig. 1.

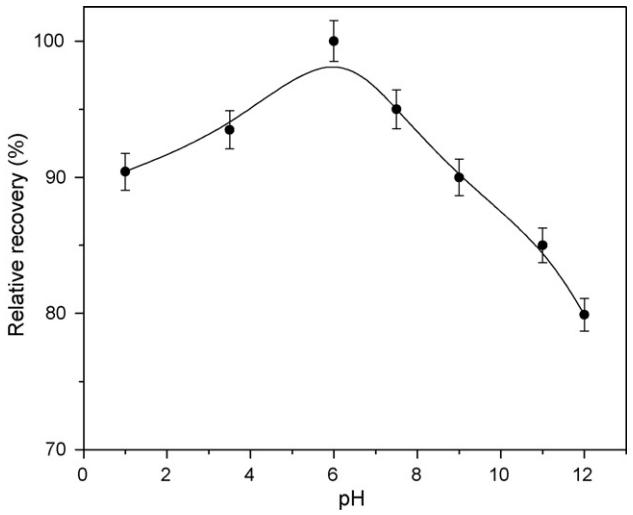

Fig. 3. pH effect on the relative recovery of 2,4,6-TCA. Extraction conditions as described in Fig. 1.

The effect of the sample pH was investigated within the pH range of 1–12 adjusting it by addition of hydrochloric acid or sodium hydroxide solutions. The results are shown in Fig. 3. Due to the 2,4,6-TCA nature, it is to be expected that the sample pH would not affect the relative recovery. However, it was observed that sample pH has a little influence on the relative recovery of the target analyte at acid and neutral pH values. The relative recovery increases ca. 10% as the pH increase between pH 1 and 6. The best relative recovery was obtained at pH 6. At higher pH values, the relative recovery decreases ca. 20% for pH 12. The sample pH could be affecting the matrix nature reducing the analytical response of 2,4,6-TCA. Therefore, the samples were adjusted at pH 6 by adding 300 μL 0.05 mol L^{-1} phosphate buffer.

3.4. Effect of extraction temperature

Temperature can affect the relative recovery of the analytical technique. It affects the analyte and organic solvent solubility in water, as well as the emulsification phenomenon due to a variation in the viscosity and superficial strength of the fluids. Thus affects the mass-transfer process. The temperature study was carried out within the temperature range of 10–80 °C (Fig. 4). The extraction procedure was the one described above. At low temperatures (<20 °C) low relative recovery values were observed. At temperatures lower than 20 °C it was difficult to get a homogeneous emulsion, resulting in a prompt phase separation. The chloroform viscosity increases affecting negatively the emulsification phenomenon [29]. Therefore, the mass-transfer process was limited to a short time, leading poor extraction efficiency, and consequently low relative recovery of 2,4,6-TCA. In the 25–55 °C range, the emulsification was easily achieved and remained invariant during the whole extraction time and the highest relative recovery of the analyte was achieved at 30 °C. At a temperature higher than 55 °C chloroform was completely dissolved into the aqueous bulk; therefore it was not possible to achieve a homogeneous emulsion. However phase separation was achieved by cooling down the tube and centrifuging it. No variations on the resulting extraction phase volume were observed. Within this temperature range the relative recovery of 2,4,6-TCA decreased notoriously. One of the reasons could be the solubility of the analyte. From the study it is possible to observe that it is important to fix the extraction temperature in order to get a stable emulsion that lead to a maximum relative recovery of the extraction technique. Therefore, the working temperature selected for further studies was 30 °C.

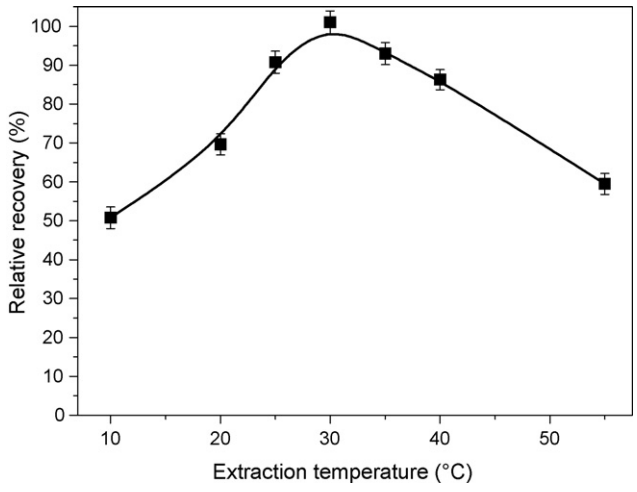

Fig. 4. Extraction temperature effect on the relative recovery of 2,4,6-TCA. Extraction conditions: sample volume, 5 mL; 150 μL 6.15 mol L^{-1} NaCl; 300 μL 0.05 mol L^{-1} phosphate buffer pH 6; extraction solvent volume, 40 μL chloroform; extraction time, 5 min; centrifugation time, 2 min. 2,4,6-TCA concentration: 1 μg L^{-1}.

3.5. Effect of shaking mode

It was interesting to compare different shaking modes to produce the emulsification since it could affect the droplet size of the emulsified phase. This phenomenon can significantly affect the contact surface of the extraction phase, and thus the mass-transfer process of 2,4,6-TCA into the organic phase. As can be seen from Fig. 5, the relative recovery of 2,4,6-TCA obtained by vigorously stirring the solution in the 1–14 min range was lower than the obtained by sonication. For shaking time higher than 14 min the relative recovery obtained for 2,4,6-TCA was comparable for both shaking modes. Sonication produced smaller droplets of organic solvent in the aqueous bulk than vigorous stirring. Therefore, 5 min sonication was selected for further studies in order to shorten the extraction procedure.

3.6. Effect of extraction and centrifugation time

Time plays an important role into the emulsification and mass-transfer phenomena. Both phenomena influence the extraction efficiency of 2,4,6-TCA, and thus their relative recovery. The extraction time interval was defined as the time elapsed between

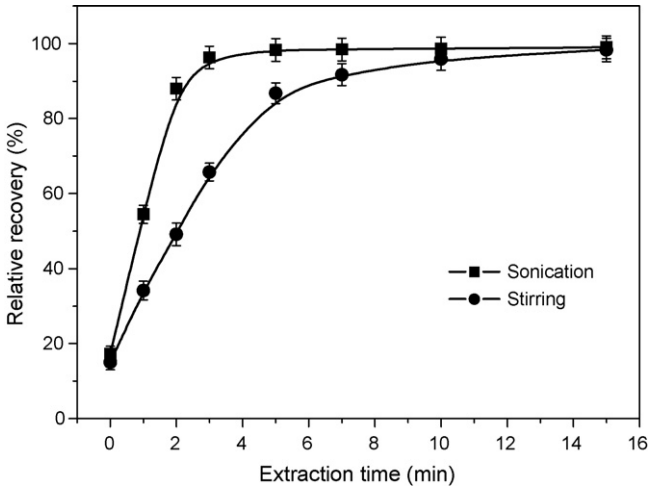

Fig. 5. Comparison of the relative recovery of 2,4,6-TCA as a function of the emulsification mode. Extraction conditions as described in Fig. 4.

extractant solvent addition and the end of the sonication stage. To determine the influence of the extraction time, it was varied within the range of 1–15 min. The extraction procedure was the one described above. It was observed that by increasing the extraction time, the relative recovery increased, reaching the maximum value at 4 min, after which remained invariant. Therefore, 5 min sonication time was chosen as working condition for further studies.

Centrifugation was required to break down the emulsion and accelerate the phase-separation process. In this way, different centrifugation times were assayed ranging from 2 to 15 min at 3500 rpm (1852.2 × *g*). Similar results were achieved in the whole time frame studied; thus the minimum time (2 min) was selected as the centrifugation time necessary to get a satisfactory biphasic system.

3.7. Analytical performance

Extraction efficiency higher than 99% was achieved when the procedure was carried out under optimum conditions. The relative recovery was determined as follows: two successive USAEME procedures were carried out over the same sample. After performing the first USAEME, the upper aqueous phase was taken and submitted to second extraction in a clean tube. Response for 2,4,6-TCA in second extracts represented less than 1% of those obtained in the first ones. The obtained EF for a sample volume of 5 mL was 555. The obtained EF was evaluated by comparison with a standard solution of 2,4,6-TCA. Considering that the extraction efficiency was higher than 99%, the EF was calculated as the ratio between the volume of extraction solvent before and after USAEME technique. The LOD of 2,4,6-TCA was calculated as three times the S/N of a sample spiked at 1 ng L^{-1}. The resulting LOD for 2,4,6-TCA was 0.2 ng L^{-1}. The precision of USAEME-GC–MS/MS was evaluated over five replicate spiked at 1 ng L^{-1}, resulting RSD 6.3%. The calibration curves linearity was investigated within the concentration range of 1–5000 ng L^{-1}, and it showed a satisfactory linearity with a coefficient of estimation (r^2) of 0.997. In order to validate the analytical methodology, a recovery study of 2,4,6-TCA at two different concentrations (5 and 25 ng L^{-1}) was carried out over the real water samples. This study led to a satisfactory robustness achieving recoveries ≥ 94% (Table 1).

3.8. Application to real samples

USAEME–GC–MS/MS was applied for determination of 2,4,6-TCA in water samples, including tap, lake and river waters as well as the surface water supplies used by the city of Mendoza. The samples were collected and immediately analyzed as described above. Since no matrix effects were observed, even in the most complex samples, quantification could be performed by external calibration using 2,4,6-TCA standard solutions prepared in chloroform spiked with BDE-47 (IS) 100 ng L^{-1}. The sample results and the recovery study were performed in triplicate (Table 1). The investigation revealed that 2,4,6-TCA concentration in the analyzed samples were below the detection limit of the proposed methodology. Fig. 6 shows the chromatograms of a lake water sample analyzed with the proposed USAEME–GC–MS/MS.

Table 1
Recovery study of 2,4,6-TCA in different water samples.

	2,4,6-TCA	
	Level found[a]	Recovery[b]
Tap water		
Tap water	nd	–
Spiked (5 ng L^{-1})	4.9 ± 0.8	98
Spiked (25 ng L^{-1})	25.1 ± 3.9	100
River water		
River water	nd	–
Spiked (5 ng L^{-1})	4.8 ± 0.7	96
Spiked (25 ng L^{-1})	24.1 ± 3.7	96
River water		
River water	nd	–
Spiked (5 ng L^{-1})	4.7 ± 0.7	94
Spiked (25 ng L^{-1})	23.9 ± 3.7	96

Extraction conditions: sample volume, 5 mL; extraction solvent, 40 μL $CHCl_3$; 150 μL 6.15 mol L^{-1} NaCl; 300 μL 0.05 mol L^{-1} phosphate buffer pH 6.0; extraction time, 5 min; centrifugation time: 2 min; extraction temperature: 30 °C.
nd: not detectable.
[a] Results expressed as $\bar{x} \pm \frac{t \cdot SD}{\sqrt{n}}$; $n = 3$; 95% confidence interval; ng L^{-1}.
[b] [(Found − base)/added] × 100.

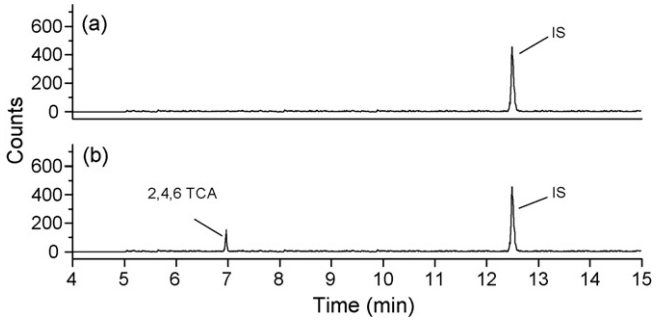

Fig. 6. Analysis of lake water sample. EIC for *m*/*z* 195, 197, 324, 326 and 328. (a) Sample spiked at 100 ng L^{-1} of BDE-47 and (b) sample spiked with 100 ng L^{-1} BDE-47 and 5 ng L^{-1} of 2,4,6-TCA.

3.9. Comparison of USAEME–GC–MS/MS with other analytical methodologies

The analytical performance of USAEME–GC–MS/MS for 2,4,6-TCA determination in water samples was compared with other analytical methodologies previously reported (Table 2). It can be observed that the analytical performance for USAEME–GC–MS/MS is comparable with methodologies previously used for 2,4,6-TCA determination. Only SBSE–GC–MS/MS showed lower LODs than USAEME but the mean RSDs values were higher. The extraction

Table 2
Determination of 2,4,6-TCA in water samples by using different analytical methodologies.

Methodology	LOD (ng L^{-1})	Linear range (ng L^{-1})	RSD (%)	Extraction time (min)	References
SPME–GC–MS/MS	0.34	1.0–500	20.8	30	[30]
PT–GC–MS	0.40	10–200	6.2	25	[14]
SPME–PTV–GC–MS	0.32	0.5–50	6.9	30	[31]
SBSE–GC–MS/MS	0.03	0.4–500	13.3	60	[11]
SPME–GC–ECD	0.70	5–80	3.4	30	[15]
USAEME–GC–MS/MS	0.20	1.0–5000	6.3	5.0	This work

SPME–GC–MS/MS: solid-phase microextraction and gas chromatography–tandem mass spectrometry. PT–GC–MS: purge-and-trap and gas chromatography–mass spectrometry. SPME–PTV–GC–MS: solid-phase microextraction–programmable temperature vaporizer and gas chromatography–mass spectrometry. SBSE–GC–MS/MS: stir bar sorptive extraction and gas chromatography–tandem mass spectrometry.

time in USAEME is shorter because the extraction equilibrium is established within a few minutes in comparison to SPME and SBSE. In SPME technique is required a longer extraction time since the partitioning equilibriums between liquid–gas phase and gas–solid phase are reached slowly. Furthermore, USAEME employs simple and inexpensive equipment and so it is applicable for most of the analytical laboratories. Additionally, it is important to point out that USAEME is a low organic solvent-consuming extraction technique, which turns it into a low cost and environmentally friendly technique. As a result, USAEME is a sensitive, rapid, inexpensive and reproducible technique.

4. Conclusions

The application of the proposed analytical methodology based on USAEME proved to be effective for determination of 2,4,6-TCA at concentrations considered to produce taste and odour in water supplies and reservoirs. Under optimized working conditions, a high EF was obtained allowing to reach detection limit in the order of low nanogram per liter with an acceptable precision, suitable for real world applications. The robustness of the methodology was proved by the recovery study carried out over the real samples. Matrix effects were not observed, even in the most complex samples. This fact allowed performing the quantification by using the external standard prepared in chloroform and ccontributed to simplify the 2,4,6-TCA determination routine, improving the sample throughput of the analytical methodology. Its simplicity and swiftness make it a convenient alternative for trace analysis by GC. All these results disclosed that USAEME is a sensitive, rapid and reproducible technique. USAEME was finally applied to the analysis of several real water samples including tap water, lake water and river water; none of them reported the presence of 2,4,6-TCA.

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References

[1] A. Diaz, C. Fabrellas, F. Ventura, M.T. Galceran, J. Agric. Food Chem. 53 (2005) 383.
[2] D. Benanou, F. Acobas, M.R. Deroubin, F. David, P. Sandra, Anal. Bioanal. Chem. 376 (2003) 69.
[3] S.E. Jensen, C.L. Anders, L.J. Goatcher, T. Perley, S. Kenefick, S.E. Hrudey, Water Res. 28 (1994) 1393.
[4] C.P. Dionigi, D.F. Millie, A.M. Spanier, P.B. Johnsen, J. Agric. Food Chem. 40 (1992) 122.
[5] S.D. Richardson, Trends Anal. Chem. 22 (2003) 666.
[6] A. Montiel, S. Rigal, B. Welte, Water Sci. Technol. 40 (1999) 171.
[7] S. Karlsson, S. Kaugare, A. Grimvall, H. Boren, R. Savenhed, Water Sci. Technol. 31 (1995) 99.
[8] L. Malleret, A. Bruchet, J. Am. Water Works Assoc. 94 (2002) 84.
[9] A. Díaz, F. Ventura, M.T. Galceran, J. Chromatogr. A 1064 (2005) 97.
[10] L. Zhang, R. Hu, Z. Yang, J. Chromatogr. A 1098 (2005) 7.
[11] L. Maggi, A. Zalacain, V. Mazzoleni, G.L. Alonso, M.R. Salinas, Talanta 75 (2008) 753.
[12] A.J. Hassett, E.R. Rohwer, J. Chromatogr. A 849 (1999) 521.
[13] B.G. Brownlee, G.A. MacInnis, L.R. Noton, Environ. Sci. Technol. 27 (1993) 2450.
[14] A. Salemi, S. Lacorte, H. Bagheri, D. Barcelo, J. Chromatogr. A 1136 (2006) 170.
[15] P.B.M. Pinheiro, J.C.G.E. Da Silva, Anal. Bioanal. Chem. 382 (2005) 341.
[16] P.B. Johnsen, J.C.W. Kuan, J. Chromatogr. A 409 (1987) 337.
[17] S. Jönsson, T. Uusitalo, B. Van Bavel, I.B. Gustafsson, G. Lindström, J. Chromatogr. A 1111 (2006) 71.
[18] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.
[19] K.E. Rasmussen, S. Pedersen-Bjergaard, Trends Anal. Chem. 23 (2004) 1.
[20] A. Tankeviciute, R. Kazlauskas, V. Vickackaite, Analyst 126 (2001) 1674.
[21] J. Wu, K.H. Ee, H.K. Lee, J. Chromatogr. A 1082 (2005) 121.
[22] J. Regueiro, M. Llompart, C. Garcia-Jares, J.C. Garcia-Monteagudo, R. Cela, J. Chromatogr. A 1190 (2008) 27.
[23] M.D. Luque de Castro, F. Priego-Capote, Talanta 72 (2007) 321.
[24] J. Regueiro, M. Llompart, E. Psillakis, J.C. Garcia-Monteagudo, C. Garcia-Jares, Talanta 79 (2009) 1387.
[25] S. Ozcan, A. Tor, M.E. Aydin, Anal. Chim. Acta 647 (2009) 182.
[26] A.R. Fontana, R.G. Wuilloud, L.D. Martínez, J.C. Altamirano, J. Chromatogr. A 1216 (2009) 147.
[27] M.D. Luque de Castro, F. Priego-Capote (Eds.), Ultrasound Assistance to Analytical Heterogeneous Liquid–Liquid Systems. Analytical Applications of Ultrasound, Elsevier, Amsterdam, The Netherlands, 2007.
[28] T.J. Mason, J.P. Lorimer, Applied Sonochemistry: Uses of Power Ultrasound in Chemistry and Processing, Wiley VCH Verlag GmbH, Weinheim, 2002.
[29] D.W. Green, R.H. Perry (Eds.), Perry's Chemical Engineers' Handbook, 8th ed., McGraw-Hill, New York, 2008.
[30] Y.H. Sung, T.Y. Li, S.D. Huang, Talanta 65 (2005) 518.
[31] L. Zhang, R. Hu, Z. Yang, Water Sci. Technol. 54 (2006) 335.