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Rapid analysis of triclosan in water samples using an in-tube ultrasonication assisted emulsification microextraction coupled with gas chromatography-electron capture detection

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In this study, a new in-tube based ultrasound-assisted emulsification microextraction (IT-USAEME) technique coupled with gas chromatography-micro-electron capture detection (GC-μECD) was developed for the efficient and rapid analysis of triclosan in environmental water samples. In this extraction procedure, the aqueous sample was taken in an indigenously fabricated home-made glass extraction device (an 8 mL glass tube inbuilt with a self-scaled capillary tip) and extraction solvent (low density organic solvent) was added to it followed by ultrasonication. After extraction, the upper extractant layer was narrowed into the self-scaled capillary tip by pushing the plunger plug; thus making the collection and measurement of the upper organic solvent layer simple and convenient. Parameters affecting the extraction efficiency such as selection of extraction solvent, extraction solvent volume, ultrasonication time, pH and ionic strength were thoroughly investigated and optimized. Under optimal conditions, the method showed good linearity in the concentration range from 20–2000 ng L^{-1} with a correlation coefficient of 0.9982 for the target analyte. The limit of detection was 4 ng L^{-1} and the enrichment factor obtained was 331. The method was validated with real water samples and the relative recoveries of environmental water samples ranged between 91.2 and 97.3% and relative standard deviations ranged between 2.8 and 5.4%, making the proposed method highly reliable. Moreover, the present approach avoids the usage of chlorinated organic extraction solvents and derivatization processes for triclosan determination. The proposed method provides a simple, rapid, sensitive, low cost, easy to handle (in-tube set-up for USAEME) and eco-friendly procedure to determine triclosan in aqueous samples.

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1 Introduction

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol, TCS) has found a place in many everyday household products for its role as a antimicrobial active ingredient in personal care products, such as toothpastes, hand cleansers, air fresheners and deodorants. It is also used as a material preservative in products including adhesives, floor wax emulsions, toys, sealants and a wide variety of other products.[1] The incorporation of TCS into this vast array of products has resulted in its discharge into surface waters.[2] Since TCS bears structural similarity to highly toxic contaminants such as dioxins or hydroxylated polychlorinated biphenyls, there is a possibility of their conversion into these hazardous compounds.[3,4] *In vivo* studies have showed that TCS affects thyroid hormone homeostasis in rats.[5] TCS is also toxic to aquatic species such as algae, daphnia and fish.[6] Hence, TCS has been categorized as a high priority pollutant by the United States Environmental Protection Agency (USEPA).[7] Considering the above-mentioned toxic effects, it is necessary to develop a rapid, sensitive and simple method for the determination of TCS in environmental water samples.

Both high performance liquid chromatography (HPLC)[8] and gas chromatography (GC)[9] techniques have been used for separation and identification of TCS. Many different analytical methods have been reported for the determination of TCS in water samples based on a sample preconcentration step followed by the selective and sensitive analysis of the target analyte using mass spectrometry, generally in combination with GC. Most of the sample preparation methods for GC analysis usually require a derivatization step[9,10] due to the highly polar nature of TCS, but GC is still the method of choice for TCS determination,

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because of the attainment of low quantification limits.[11] However, in the present method, a GC method that prevents derivatization has been introduced for determining TCS by GC-micro-electron capture detection (μECD).

Sample pretreatment procedures are usually vital to improve the sensitivity and selectivity of analytical methods. Conventional sample preparation methods for TCS analysis include liquid–liquid extraction (LLE)[12] and solid-phase extraction (SPE).[13] But their disadvantages include consumption of large volumes of toxic solvents and being time-consuming. They have been significantly replaced by more efficient and miniaturized techniques like solid-phase microextraction (SPME),[14] hollow-fiber liquid-phase microextraction (HF-LPME),[15] stir bar sorptive extraction (SBSE),[16,17] and dispersive liquid–liquid microextraction (DLLME).[18] Of these techniques, the disadvantages of SPME and SBSE include requirement of expensive and special apparatus with a limited lifetime and sample carry-over problem. Long extraction time, instability of the microdrop, sometimes low precision, usage of dispersive solvents and toxic chlorinated organic extraction solvents are some of the disadvantages of HF-LPME and DLLME techniques.[19–21] Recently, the use of ultrasound-generated emulsions, developed by Reguerio, has gained popularity in improving the efficiency of DLLME as an ultrasound-assisted emulsification microextraction (USAEME) technique.[22] Ultrasonic radiation is a powerful tool for the acceleration of the mass transfer process of the analytes between the aqueous sample solution and the water-immiscible extraction solvent, resulting in an increase in the extraction efficiency in a short time.[23] In this method, a micro-liter amount of a water-immiscible extraction solvent is dispersed into water sample by ultrasound assisted emulsification without the usage of a dispersive solvent.[24] This developed procedure has many merits such as excellent enrichment factors, simplicity, stability, ease of operation, low cost and micro-liter consumption of organic solvents.[25] Usually, a screw cap glass centrifugation tube is often used as the extraction device for USAEME. However, the collection and measurement of micro-liter volumes of the separated organic extraction phase were difficult because of the wide diameter of the glass tube, making the thin layer of extract difficult to retrieve, with a relatively long extraction time with poor precision.

A few approaches have been reported for introducing extraction devices or vessels into classical DLLME or USAEME methods that allow the use of organic extraction solvents, either by using a narrow-necked glass tube,[26] or by using a glass vial or a soft polyethylene Pasteur pipette.[27,28] These devices, however, pose some practical inconvenience which can only be experienced during use. Thus, the accurate recovery of the extraction solvent after USAEME remained a challenge. More recently, we demonstrated a very simple and convenient in-syringe based USAEME method by using a glass microsyringe adopted with a scaled micro-capillary tube as an extraction device, which is widely commercially available.[29] Thus far, there has been no report related to the application of USAEME to extract TCS from water samples using a low density organic extraction solvent which is determined by GC-ECD without any prior derivatization process.

In this study, for the first time, we demonstrate a new in-tube (home-made glass tube device) based USAEME technique using low-density organic solvents for the extraction and preconcentration of TCS from environmental water samples by GC-μECD, providing the combined benefits of the home-made glass extraction device, low-density organic solvents and USAEME. This paper aims to present a new extraction alternative that provides a simple, fast, accurate and hassle free way to collect less toxic low-density organic extraction solvent from an extraction unit which avoids the inconvenient, time consuming and cumbersome procedures. All the variables affecting the IT-USAEME procedure were intensively studied, and the analytical figures of merit were established. Applicability of the proposed method was examined by extending the developed method to environmental water samples.

2 Experimental

2.1 Reagents and solutions

All chemicals used in this work were of ACS reagent grade. Triclosan (99.5%), toluene, decane, isooctane and 1-octanol were purchased from Merck Chemicals (Darmstadt, Germany). Sodium chloride (NaCl) was purchased from Showa (Tokyo, Japan). HPLC-grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) were also purchased from Merck (Darmstadt, Germany). Ultra-pure water for all aqueous solutions was produced in the laboratory using a Barnstead Nanopure water system (Barnstead, New York, USA). Stock solution (1 mg L^{-1} of TCS) was prepared by dissolving the analyte in methanol and stored in brown glass bottles with polytetrafluoroethylene (PTFE)-lined caps and kept at 4 °C. Working standard solutions were obtained daily by diluting the stock solutions with ultra-pure water. High purity nitrogen (99.9995%) used as the carrier gas was obtained from a local supplier (Lien-Hwa, Taichung, Taiwan).

2.2 Instrumentation

The GC used in this work was an Agilent 6890N (Agilent Technologies, Santa Clara, CA, USA), equipped with a split/split-less injector and a micro-electron capture detector (μECD, 63Ni). Compounds were separated on a fused silica DB-608 capillary column (30 m × 0.25 mm i.d., 0.25 μm thick film) (Agilent Technologies, Palo Alto, CA, USA). Nitrogen was used both as the carrier gas and makeup gas at flow rates of 2.0 and 50 mL min^{-1}, respectively. The gas chromatograph was operated in split-less mode with an injector temperature of 280 °C. The oven temperature was initially maintained at 160 °C for 1 min, programmed at 25 °C min^{-1} to 280 °C and held for 5 min, and finally at 35 °C min^{-1} to 300 °C held for 3 min. The separated species were measured using a μECD held at 330 °C. Agilent Chemstation 4.01 (Agilent Technologies) was used for instrument control and data analysis.

2.3 IT-USAEME set-up and procedure

The experimental setup of IT-USAEME has been demonstrated in Fig. 1A. IT-USAEME consisted of the following steps: 5 mL of

sample solution containing 2.5% NaCl was taken in an 8 mL home-made glass tube (Fig. 1a and b). Then, 20 μL of 1-octanol (as the extraction solvent) was injected into the sample solution with the help of a 50 μL microsyringe (Fig. 1c). After that, the extraction device was sealed with a rubber plunger (Fig. 1d) and ultrasonicated at an operating frequency of 43 kHz and output power of 80 W. A turbid solution was formed in the process of ultrasonication due to the dispersion of fine 1-octanol droplets into the sample (Fig. 1e). After 30 seconds of ultrasonication, the sealed extraction device was centrifuged at 3200 rpm for 3 min with a DSC-158 centrifuge (Digi-System Laboratory Instruments Inc, Taiwan) to separate the extraction solvent from the aqueous sample (Fig. 1f). Once the phase separation occurred, the rubber cap on the capillary tip was removed and the upper organic layer could be narrowed into the self-scaled capillary tip by gently pushing the rubber plug. Finally, the extractant phase was easily measured and recovered using a 10 μL glass microsyringe and one micro-liter was injected into the GC-μECD system for analysis (Fig. 1g).

2.4 Calculation of extraction recovery and enrichment factor

Extraction recovery (ER)[21,27–29] was calculated based on the following equation:

$$\mathrm{ER}\% = (C_{\mathrm{og}}V_{\mathrm{og}})/(C_0V_{\mathrm{aq}}) \times 100$$

where C_{og} and C_0 are the concentration of the analyte in the collected organic phase and initial concentration of the analyte

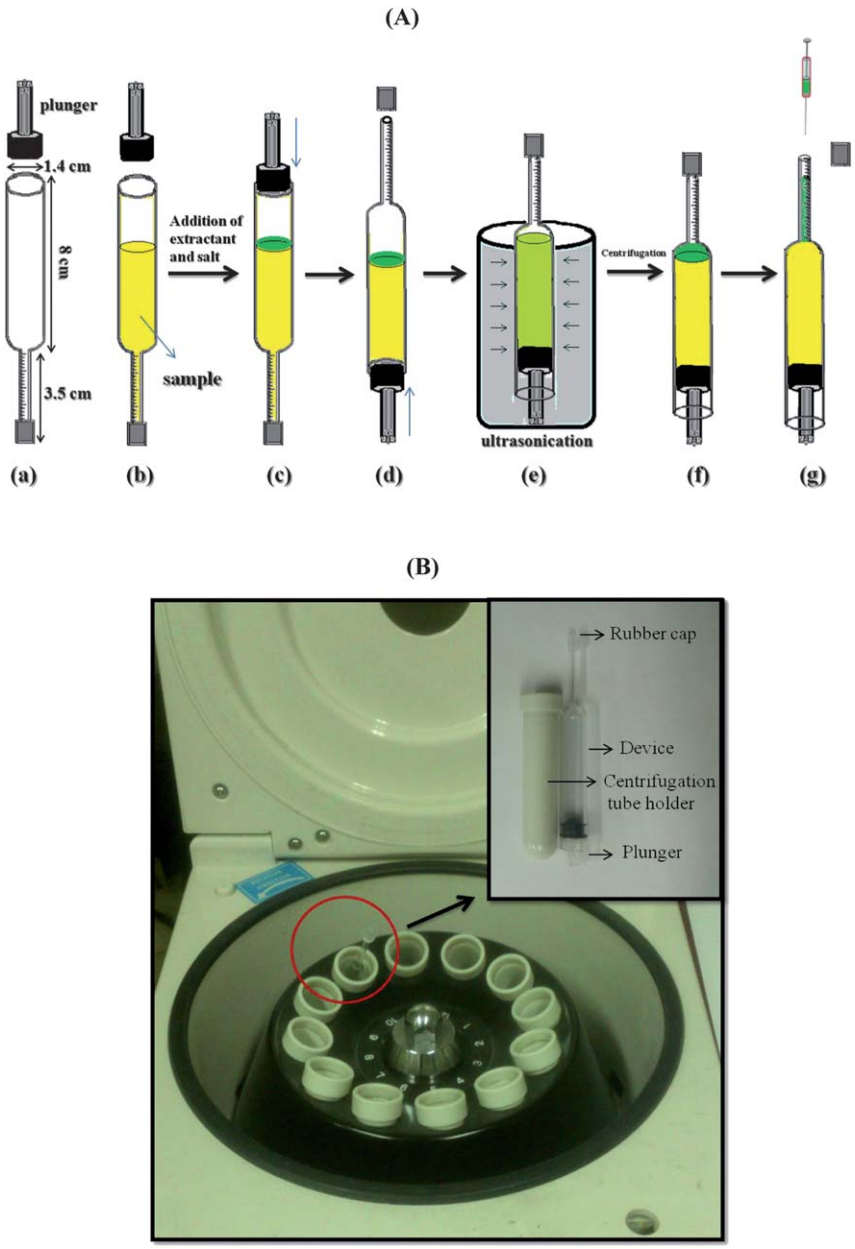

Fig. 1 (A) A schematic set-up of the proposed in-tube based USAEME technique and (B) actual photograph of the proposed in-tube extraction device and its centrifugation process.

in the aqueous sample; V_{og} and V_{aq} are the volumes of the floating phase and aqueous sample, respectively.

Enrichment factor (EF)[21,27–29] was calculated as the ratio of concentration of the analyte in the collected organic phase (C_{og}) and initial concentration of the analyte in the aqueous sample (C_0).

$$EF = C_{og}/C_0$$

3 Results and discussion

In the present IT-USAEME study, the applicability of organic solvents that have lower density than water was examined and an 8 mL indigenously fabricated home-made glass tube (8 cm length and 1.4 cm internal diameter) inbuilt with a self-scaled (3.5 cm length) capillary tip (capillary tip was covered with a rubber cap in order to avoid any loss of sample solution during the extraction process) was employed to overcome the problem of collection of the separated organic solvent on the surface of the water samples after extraction. The design of the home-made glass tube and extraction procedure steps are illustrated in Fig. 1A. The extraction device was sealed with a rubber plunger (rubber cap on the capillary tip was removed while inserting the rubber plunger into the extraction device in order to avoid trouble during plunger movements) (Fig. 1d). Also, the present extraction device shows good stability during centrifugation because the total length of the extraction device (8 cm tube + 3.5 cm capillary tube + 3 cm of plunger) is 14.5 cm and the width is 1.4 cm which is more fit and compatible with the centrifuge tube holder in the centrifuge instrument (Fig. 1f). So, no other support or modification in the centrifuge (Fig. 1B) was needed to ensure its integrity during the centrifugation process. By using the newly designed home-made glass tube, the usage of low density solvents in IT-USAEME is now made possible in a easy to handle and inexpensive way. Several factors influenced the extraction efficiency of the IT-USAEME technique including the selection of extraction solvent, extraction solvent volume, ultrasonication time, sample pH and effect of ionic strength. Therefore, we explored the effect of each of these variables on the extraction of triclosan in water samples.

3.1 Selection of the extraction solvent

Selection of a suitable extractant for USAEME is limited by several characteristics that are necessary for emulsification in the presence of ultrasonic radiation. For practical purposes, it is necessary that the extraction solvent has good extraction ability, low water solubility, lower density than water and excellent gas chromatographic behavior.[25–29] Taking into account these exigencies, four organic solvents including toluene, 1-octanol, decane and isooctane were investigated. The extraction recovery of TCS using different solvents is shown in Fig. 2 and it can be inferred that 1-octanol has higher extraction efficiency than toluene, decane and isooctane. Therefore, 1-octanol was selected as the extraction solvent for further studies.

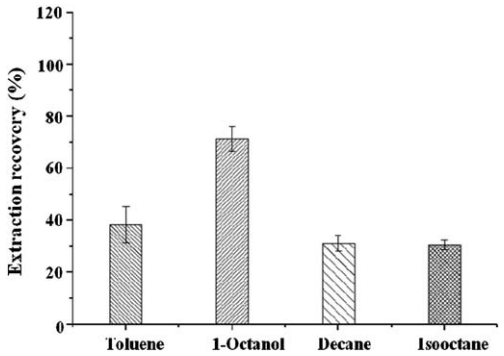

Fig. 2 Relative extraction efficiency for different extraction solvents for 200 ng L^{-1} of TCS in water. *Experimental conditions*: sample volume: 5 mL; spiked concentration: 200 ng L^{-1}; sample pH: 5; ultrasonication time: 30 s; centrifugation time: 3 min; and $n = 5$.

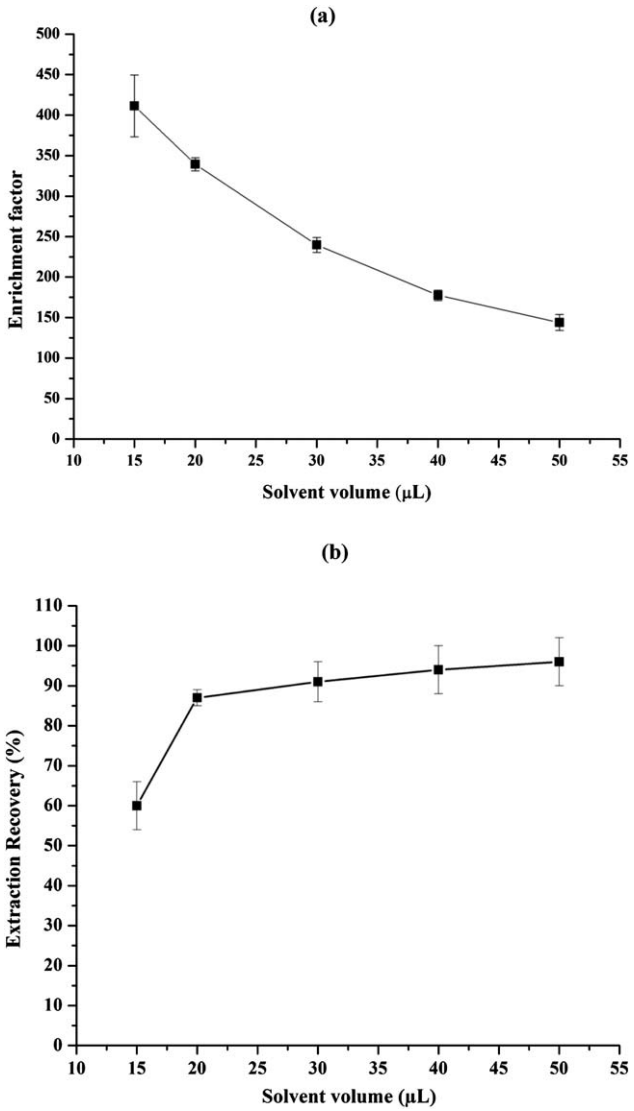

Fig. 3 Effect of extraction solvent volume on (a) enrichment factor and (b) extraction recovery, by the proposed technique. Experimental conditions are the same as for Fig. 2.

3.2 Effect of extraction solvent volume

One of the most important steps in method optimization of IT-USAEME was the effect of the volume of extraction solvent. From the equilibrium of an analyte between two liquid phases in an extraction, the solvent volume directly affected the extraction efficiency of the analyte. In order to obtain the highest extraction efficiency, the volume of the extraction solvent was studied within a volume range of 15–55 μL. It can be inferred from Fig. 3a that the enrichment factors decreased with increasing volume of 1-octanol from 15 to 55 μL due to the decrease in concentration of the target analyte in the extraction solvent, thereby causing a dilution effect.[29,30] 15 μL of 1-octanol showed the maximum enrichment factor with poor RSD. However, the extraction recovery of TCS increased with increasing quantity (15 to 55 μL) of 1-octanol (Fig. 3b). Hence in order to balance both enrichment factor and extraction recovery (based on repeatability), 20 μL of 1-octanol was chosen for the IT-USAEME of TCS.[29]

3.3 Effect of ultrasonication time

Ultrasonication time plays an important role in emulsification and mass transfer phenomena, as it influences the extraction efficiency to a great extent.[31] The effect of ultrasonication time was studied in the present IT-USAEME procedure and it was varied within the range of 15–90 seconds. It can be observed from Fig. 4 that extraction recovery increased with extraction time until 30 seconds at which maximum extraction occurred and then remained constant. Therefore, 30 seconds was chosen as the extraction time for further studies.

3.4 Effect of pH

The effect of sample pH was investigated within the pH range of 3–9 by adjusting it through the addition of hydrochloric acid or sodium hydroxide solutions. It can be observed from Fig. 5 that the extraction recoveries of TCS decreased significantly when the pH of the aqueous solution was greater than 6, probably because changing the pH of the sample solution results in deprotonation of TCS (the predomination of the phenolate form under conditions leading to alkalinity), which can significantly affect its solubility in the aqueous phase and decrease the amount of TCS in the extractant phase since TCS is a weak acid (pK_a = 7.9).[2,32] Based on the above observations, pH 5 was selected as the optimum extraction condition for further experiments.

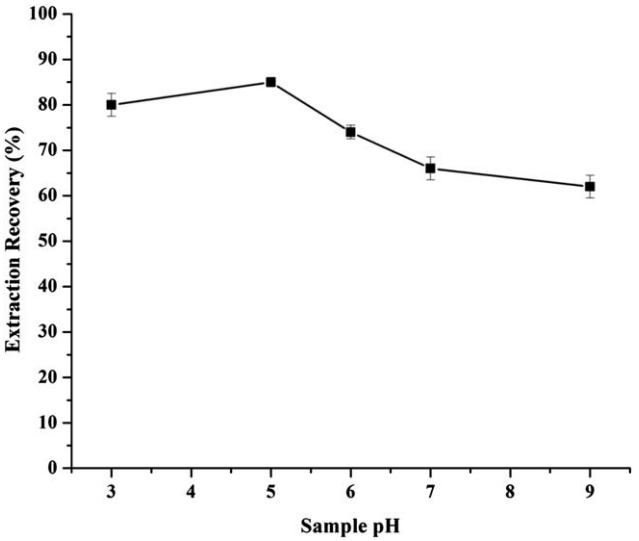

Fig. 5 Effect of sample pH on the extraction efficiency by the proposed technique. Experimental conditions are the same as for Fig. 2 except sample pH. Extraction solvent volume – 20 μL.

3.5 Effect of ionic strength

Considering that the salting out effect had been used in USAEME to improve the extraction of analytes from water

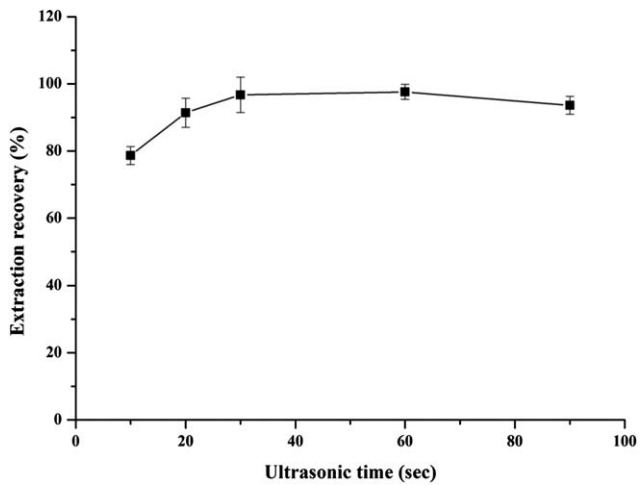

Fig. 4 Effect of ultrasonication time on the extraction efficiency by the proposed technique. Experimental conditions are the same as for Fig. 2 except ultrasonication time. Extraction solvent volume – 20 μL.

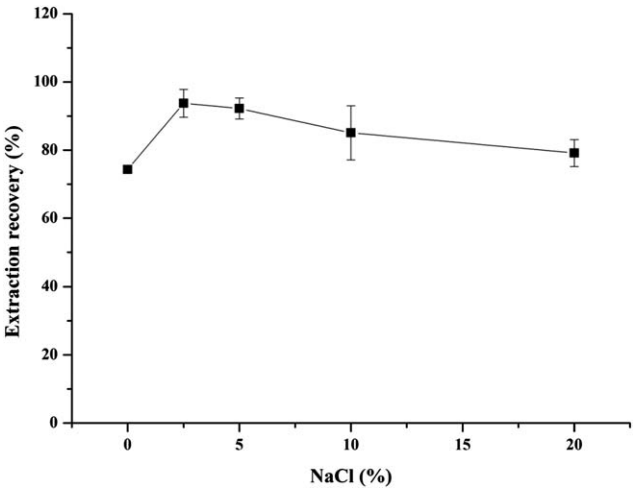

Fig. 6 Effect of salt addition on the extraction efficiency by the proposed technique. Experimental conditions are the same as for Fig. 2. Extraction solvent volume – 20 μL.

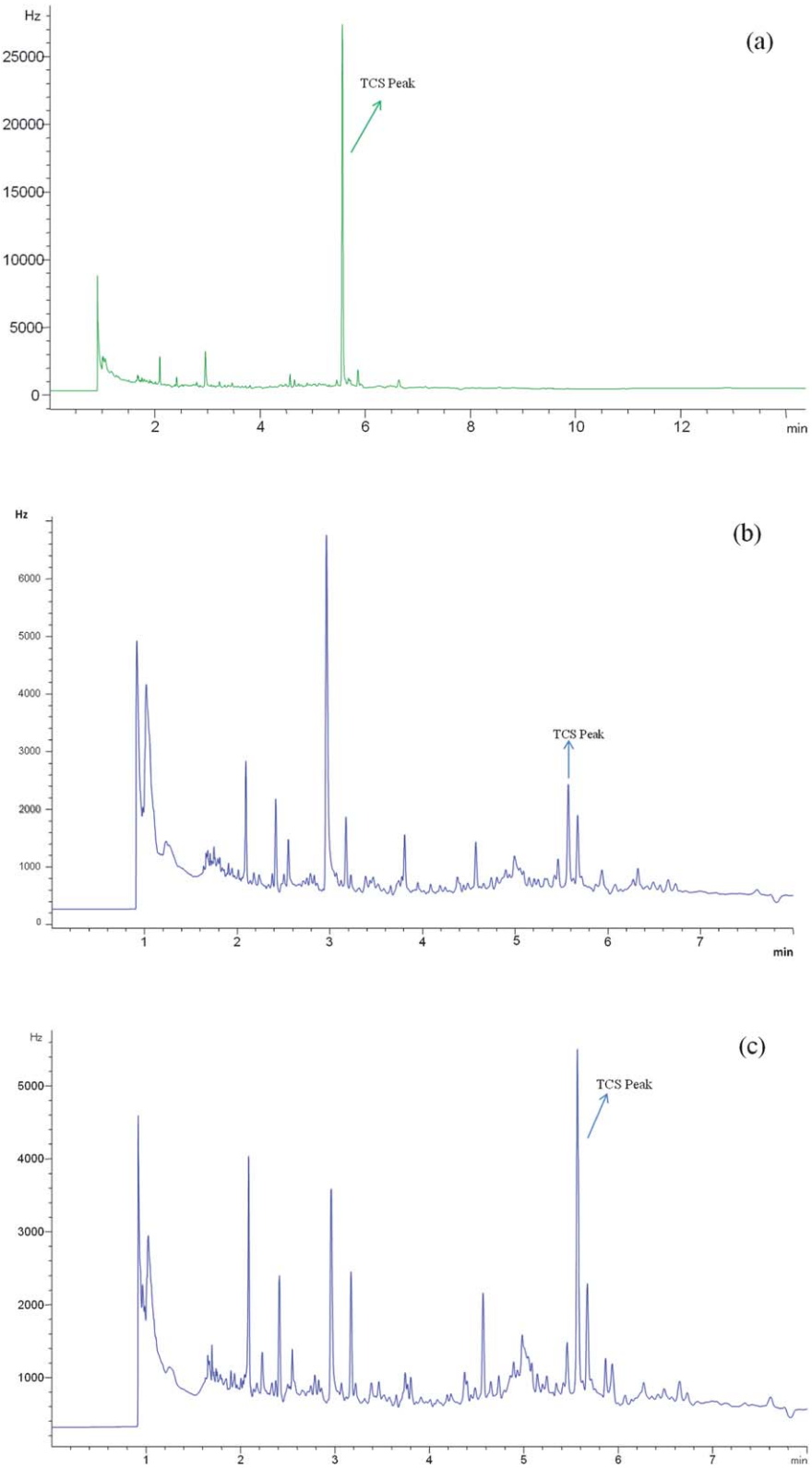

Fig. 7 Typical GC-μECD chromatograms of TCS by the proposed technique under optimal experimental conditions: (a) ultra-pure water sample (spiked with 200 ng L^{-1} of TCS), (b) blank river water sample (non-spiked), and (c) river water sample (spiked with 50 ng L^{-1} of TCS).

samples, different amounts of sodium chloride in the range of 0–20% (w/v) were investigated in the present IT-USAEME procedure. According to the results shown in Fig. 6, the increase of NaCl from 0 to 2.5% (w/v) led to an obvious increase in extraction recovery because the salting-out effect decreased the solubility of the analytes in water and therefore increased the

concentration of analytes in the extractant phase.[33] However, the extraction recovery slightly decreased when the concentration of NaCl was increased beyond 2.5%. Considering all these factors, 2.5% NaCl was added for further experiments.

3.6 Effect of centrifugation time

A centrifugation process was needed to break down the emulsion and accelerate phase separation. Centrifugation times were tested at 3200 rpm in the range of 1–10 min. The experimental results indicated that the extraction efficiency increased when the centrifugation time was increased from 1 to 3 min. No obvious changes were observed when the time was further increased to 10 min. Based on the above observations, 3 min was selected as the optimum centrifugation time for further experiments.

3.7 Evaluation of method performance

Under the above-mentioned optimized conditions (IT-USAEME method), linear dynamic ranges, correlation coefficient (r), limits of detection (LODs), precision (in terms of relative standard deviation (RSD)) and enrichment factors were investigated. Calibration curves were plotted using 7 spiking levels of TCS in the concentrations ranging from 20 to 2000 ng L^{-1} which shows good linearity with a correlation coefficient of 0.9982 and the correlation equation was $Y = 94\ 589x + 2248$. For each level, five replicate extractions were performed under optimum conditions. A typical chromatogram of the spiked aqueous sample (200 ng L^{-1}) that was obtained under optimum conditions is demonstrated in Fig. 7(a). The LOD value was calculated based on the signal to noise ratio of three ($LOD = 3 \times S_b/m$, where S_b is the standard deviation of blank and m is the slope of the method calibration curve),[21–29] which was 4 ng L^{-1}. The enrichment factor was calculated as the ratio of final concentration of the analyte in the organic phase to its concentration in the original solution (at 200 ng L^{-1} of TCS) under optimal conditions and it was 331. The precision of the proposed IT-USAEME-GC-μECD method was evaluated in terms of repeatability (RSD% < 4.3, $n = 5$) and reproducibility (RSD% < 4.9, $n = 5$) at 200 ng L^{-1} of TCS.

3.8 Application to real water samples

Applicability of the proposed method was evaluated for the extraction of target TCS in real water samples. River water samples and lake water samples were collected from the agricultural district of Dali (Taichung City, Taiwan) and were filtered with 0.45 μm cellulose acetate membrane filters in order to eliminate any fine particulates and debris in the water samples. Then, pH of the samples was adjusted to 5 and stored at 4 °C until analysis. Blanks of the real water samples were run to determine the presence of target analytes. Experimental results showed that 0.038 μg L^{-1} TCS was detected in the river water samples. The real samples were spiked at concentrations of 0.05, 0.8 and 1.6 ng mL^{-1} by spiking TCS standard solution into the real water samples and the results are summarized in Table 1 and the non-spiked and spiked river water chromatograms by the proposed method are shown in Fig. 7(b) and (c). Relative recoveries of TCS in all the real water sample solutions were calculated by subtracting the measured quantity of the sample from the measured quantity of the spiked sample, divided by the spiked quantity and recoveries varied from 91.2–97.3% with 2.8–5.4% RSD for the samples spiked with 0.05, 0.8 and 1.6 ng mL^{-1} TCS respectively, thus proving that the represented method was reliable and convenient for the fast determination of trace amounts of TCS in various real water samples.

3.9 Comparison of the present method with other reported methods

The analytical performance of the presented method was compared with other microextraction methods such as SPME, SBSE, HF-LPME and DLLME.[14,15,18,34,35] The respective LOD, sample volume and extraction time of each method are summarized in Table 2. As can be seen from the table, advantages over other methods include lowest extraction time and sample volume in comparison with other methods, good linear ranges and precisions. Moreover, 1-octanol is used as the extraction solvent, thus preventing the use of toxic chlorinated solvents.

Table 2 Comparison of the proposed method with other methods

Method	LOD (ng L^{-1})	Sample volume (mL)	Total extraction time (min)	Ref.
Online SPME-LC-UV	1	10	60	34
SBSE-GC-MS	5	10	120	35
DLLME-GC-MS/MS	2	10	5	18
HF-LPME-GC-MS	20	10	20	15
HS-SPME-GC-MS/MS	6.5	10	15	14
IT-USAEME-GC-μECD	4	5	3.5	Proposed method

Table 1 Analytical results and recoveries of TCS in real samples by the proposed method

		Spiked concentration					
		0.05 μg L^{-1}		0.8 μg L^{-1}		1.6 μg L^{-1}	
Sample	Non-spiked (μg L^{-1})	Recovery (%)	RSD (%) ($n = 3$)	Recovery (%)	RSD (%) ($n = 3$)	Recovery (%)	RSD (%) ($n = 3$)
River water	0.038	94.3	5.4	91.2	2.8	97.3	5.2
Lake water	Not detectable	93.8	4.1	92.9	3.8	96.4	3.1

4 Conclusion

In this work, a novel IT-USAEME method combined with GC-μECD has been introduced for the determination of TCS in environmental water samples. 1-Octanol (low density solvent) was used as the extraction solvent instead of toxic halogenated solvents. The method also avoided the derivatization procedure and usage of dispersion solvents, thus making the extraction process easy to perform. The IT-USAEME-GC-μECD method with the proposed in-tube device showed enhanced extraction efficiency with good precision (because of accurate measurement of the extraction solvent by the proposed device) for the enrichment of TCS from environmental aqueous samples. Moreover, the presented extraction device provides a simple, fast, accurate and hassle free way to collect less toxic low-density organic extraction solvents which avoids the inconvenient, time consuming and cumbersome procedures. In addition, it has many merits such as rapidity, simplicity, sensitivity and being inexpensive and is an environmentally friendly method for the analysis of TCS in aqueous samples.

Acknowledgements

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