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Anele Mpupa, Geaneth P. Mashile, Philiswa N. Nomngongo*

Vortex assisted-supramolecular solvent based microextraction coupled with spectrophotometric determination of triclosan in environmental water samples

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Abstract: A simple, fast and environmental friendly vortex assisted-supramolecular solvent based microextraction (VA-SSME) method was developed for the preconcetration of triclosan in wastewater prior to UV spectrophotometric determination. To achieve maximum sensitivity and accuracy for the target analyte, the experimental parameters affecting the VA-SSME procedure were optimized using response surface methodology (RSM). Under optimised conditions, the correlation coefficient (R^2) and recoveries were 0.9994 and 100.31-118.5%, respectively. The intra-day (repeatability) and inter-day (reproducibility) precisions expressed in terms of relative standard deviation (RSD) were 2.4% and 5.2%, respectively. The preconcentration factor and limits of detection (LOD) and quantification (LOQ) were found to be 90, 0.28 μg L^{-1} and 0.92 μg L^{-1}, respectively. The developed VA-SSME/UV method was applied for the determination of triclosan in real samples collected over a period of three months. The analytical results obtained showed that triclosan was frequently detected in influent wastewater samples but was not detected in effluent samples.

Keywords: Triclosan; antimicrobial; Supramolecular solvents; UV-Vis Spectrophometry; personal care products; Response surface methodology

***Corresponding author: Philiswa N. Nomngongo:** Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa, E-mail: pnnomngongo@uj.ac.za
Geaneth P. Mashile, Anele Mpupa: Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa

1 Introduction

Triclosan (2'-hydroxy-2,4,4'-trichlorodiphenyl ether) is used as a broad-spectrum synthetic antimicrobial agent for medicated agents, toothpaste, hand and body soaps and shampoo [1,2]. Increased cases of bacterial infection have resulted in wide spread utilisation of antimicrobial agents [3]. This has elevated the concentration of these compounds in different environmental media [4]. More alarming is the evidence of transformation of these compounds into more toxic compounds such as 2,8-dichlorodibenzo-p-dioxin and 2,4-dichlorophenol [5,6]. Triclosan is regarded as an androgenic compound, moreover: it has also been found to have endocrine effects in animals and humans [7]. The United States Environmental Protection Agency (USEPA) termed triclosan a high priority pollutant as it decomposes into dioxin derivatives which are potential carcinogens [8]. Due to the potential toxicity to human and animals, the maximum permitted level of triclosan in personal care products is 0.3% (w/w) [6]. Therefore, there is a need to develop rapid, simple, selective and sensitive analytical methods for accurate quantification of trace levels of triclosan in complex environmental samples.

Consequently, several analytical methods have been developed for the assessment of triclosan in different matrices. These include high performance liquid chromatography–ultraviolet spectroscopy (HPLC-UV) [2], liquid chromatography-tandem mass spectroscopy (LC-MS/MS [9,10]), gas chromatography-mass spectroscopy (GC-MS) [11,12]. Although the aforementioned mentioned techniques have their own advantages such selectivity and high sensitivity, they often need time-consuming sample preparation steps, have a high cost of operation and suffer from complex and expensive instrumentation [13]. In addition, these analytical techniques require long analysis times and require highly skilled personnel. In contrast, spectrophotometric techniques such as UV-Vis have attractive advantages such as wide availability

of instrumentation, inherent simplicity, low cost, short analysis time, and adequate precision and accuracy [13]. In addition, these merits make the spectrophotometric techniques especially convenient for the routine analysis of different analytes.

Several spectrophotometric methods have been developed for the determination of sulfadiazine (another class of emerging pollutants) in different matrices [14-16]. The majority of the developed spectrophotometric techniques for determination of sulfadiazine are based on the formation of a detectable azo dye by the diazotization of sulfadiazine followed by its coupling with different reagents, including 8-hydroxyquinoline [17] and iminodibenzyl [18]. Triclosan has also been determined spectrophotometrically using a similar method [19]. Despite the above-mentioned advantages, the UV–VIS spectrophotometer is seriously limited by its low sensitivity. Hence, separation/preconcentration methods are required in order to carry out accurate and sensitive determinations [20]. For this reason, different sample preparation methods have been used for preconcentration of different organic pollutants prior to UV-Vis spectrophotometric determination. These sampler pretreatment techniques include dispersive liquid–liquid microextraction (DLLME) [21], solid phase extraction (SPE) [22], solid phase microextraction (SPME) [14] and supramolecular solvent-based microextraction [23], among others.

Supramolecular solvent based microextraction (SSME) uses supramolecular solvents (SUPRAS) as an extractant. SUPRAS are water immiscible liquids synthesized by self-assembly of two amphiphile solutions in a continuous phase in which self-assembly processes occur on the molecular and nano scale [24,25,26]. These supramolecular assemblies of SUPRAS lead to properties useful for extraction of inorganic and organic compounds [27]. Therefore, the principle of the SSME procedure is based on partitioning of an analyte between an alkyl carboxylic acid-based nano-structured solvent and a bulk aqueous sample [28]. SUPRAS have regions of varying polarities, providing different interactions for analytes. Hence, they are attractive solvents to replace organic solvents in analytical extractions [29]. Another feature of SUPRAS is the high concentration of amphiphiles which results in a high number of analyte binding sites. This permits high extraction efficiencies while using low extraction volumes; hence, they are frequently used in microextractions [27].

This study aims to develop a novel simple, rapid and sensitive SUPRAS (made up of decanoic acid and tricaprylymethylammonium chloride)-based microextraction and UV–VIS spectrophotometry for preconcentration and quantification of triclosan in wastewater samples. According to the authors' knowledge, the use of SUPRAS in order to improve UV-Vis spectrophometric detection capabilities for determination of triclosan or any personal care products has not been previously reported. The experimental parameters affecting the SSME procedure were optimized using response surface methodology (RSM) based on a central composite design (CCD).

2 Experimental

2.1 Reagents and standards

Triclosan (pharmaceutical secondary standard), decanoic acid, tricaprylymethylammonium chloride (Aliquat 336) and methanol were purchased from Sigma-Aldrich (St. Loius, MO, USA). A triclosan stock solution (10 mg L^{-1}) was prepared by diluting an appropriate amount of triclosan in 2 mL of methanol and diluting to 100 mL with ultra-pure water (Direct-Q® 3UV-R purifier system, Millipore, Merck). Stock triclosan was kept refrigerated. Working standard solutions were prepared daily by appropriate dilution of the stock solution with ultra-pure water.

2.2 Instrumentation

A PRO scientific VSM-3 vortex mixer (PRO scientific Inc.,) was used to vortex the samples before using an Eppendorf centrifuge 5702 (Eppendorf, Hamburg, Germany). An OHAUS starter 2100 pH meter (Pine Brook, NJ, USA) was used for pH adjustments of the reagents and to measure the pH of samples. The Shimadzu UV-2450 high performance single monochromator UV-VIS spectrophotometer (Shimadzu Corporation, Tokyo, Japan) with 5 mL quartz cuvettes and a slit width of 0.5 and wavelength of 284.8 nm was used for all sample analyses. Reference studies were carried out using an Agilent 1200 Infinity series HPLC equipped with a photodiode array detector (Agilent Technologies, Waldbronn, Germany). The chromatograms were recorded at 280 nm. An Agilent Zorbax Eclipse Plus C18 column (3.5 µm × 150 mm × 4.6 mm) (Agilent, Newport, CA, USA) was operated at an oven temperature of 25°C. The mobile phase was a mixture of 30% water (mobile phase A) and 70 % acetonitrile (mobile phase C). A flow rate of 1.00 mL min^{-1} was used throughout the analysis.

2.3 Sampling and sample collection

Influent (after sediment removal) and effluent wastewater samples were collected from Daspoort wastewater treatment plant (WWTP, Pretoria, Gauteng, South Africa). The samples were collected in pre-cleaned 500 mL glass bottles. The samples were then refrigerated at 4 °C. Samples were collected four times a month (meaning once a week) for a period of 3 months. In each week (Mondays at midday (between 11:00 and 13:00)), six samples (three influent and three effluent) were collected and analysed.

2.4 Supramolecular solvent based microextraction

A mixture of 50 µg L^{-1} decanoic acid in Aliquat-336 was prepared via stirring a mixture of the two for 5 minutes (until a clear homogenous solution formed), forming the supramolecular solvent. Different volumes (100–500 µL)of the solvent were added to centrifuge tube containing a 5 mL sample. This mixture was shaken using a vortex for a few seconds until a cloudy suspension formed. The solution was then centrifuged for a maximum of 10 minutes at 3000 rpm. After centrifuging, the top layer was recovered using a micropipette and was redissolved in 2 mL of methanol and analysed using UV-Vis spectrophotometry at 284.8 nm.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and discussion

3.1 Optimization

In order to achieve quantitative preconcetration of triclosan with the supramolecular microextraction procedure, the optimization of the most influential parameters, such as sample pH, extraction time (ET) and supramolecular solvent volume (SSV), was carried out using response surface methodology (RSM) based on a central composite design. Table 1 presents the factorial design matrix and the analytical responses (expressed as absorbance at 284.8 nm) obtained in each experiment. A Pareto chart (Figure 1) was generated for the analysis of variance (ANOVA) to explore the significance of the effects on the SSME procedure. The Pareto chart of main effects and their interactions produced is shown in Figure 1. The effect of pH and extraction time according to Figure 1 was not significant in the extraction of triclosan at the 95% confidence level. In contrast, impact of the supramolecular solvent volume (SSV) was significant at the 95% confidence level. The interaction of pH and extraction time was also statistically significant for the extraction of triclosan. The effects of extraction time and pH were only significant when considering quadratic effects, which for the purpose of the study were not considered.

Table 1: Factors and levels used in central composite for supramolecular solvent based microextraction of triclosan.

Factors	Low level (-1)	Central point (0)	High level (+1)
Sample pH	3	7	10
Extraction time (min)	2	6	10
SSV (µL)	100	300	500

Table 2: Factorial design matrix and the analytical responses (expressed as absorbance at 284.8 nm).

Exper	pH	ET (min)	SSV (µL)	Abs
1	3	2	300	1.334
2	9	2	300	1.464
3	3	10	300	1.704
4	9	10	300	2.344
5	3	6	100	0.049
6	9	6	100	0.45
7	3	6	500	1.75
8	9	6	500	1.448
9	6	2	100	1.016
10	6	10	100	0.53
11	6	2	500	1.498
12	6	10	500	1.405
13	6	6	300	0.666
14	6	6	300	0.6001
15	6	6	300	0.643
16	6	6	300	0.656
17	6	6	300	0.662
18	6	6	300	0.6729

Triclosan is a lipophilic compound with a log K_{ow} of 4.8 [30]; this means that it associates with the hydrophobic section of the supramolecular solvent during the dispersion of the solvent in the water sample [31]. In addition to the lipophilicity, the pKa of the analyte played a major role in the SSME [31]. As a result of its pKa (8.1), triclosan is stable over the pH range 4-9. The optimum pH for the extraction of 5 thus falls within the stable range of triclosan. In other words, as a result of its pKa, triclosan existed in its molecular form during the application of the method [32].

ANOVA variables of the response surface quadratic model for the absorbance of triclosan were obtained. The ANOVA results were analysed with quadratic equations for the models to illustrate the dependence of the analytical response with respect to the evaluated main effects [33]. The response surfaces together with quadratic equations

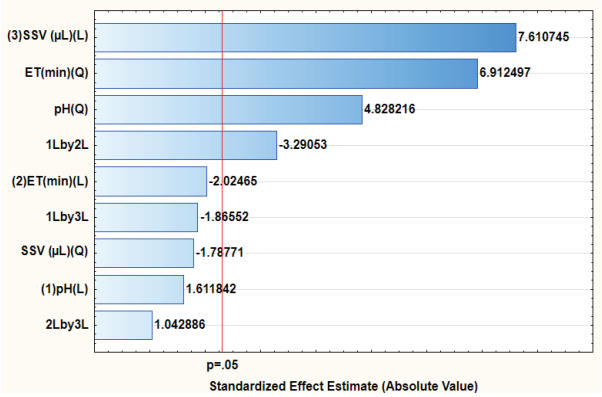

Figure 1: Pareto chart of standardized effects for variables in the preconcentration of triclosan.

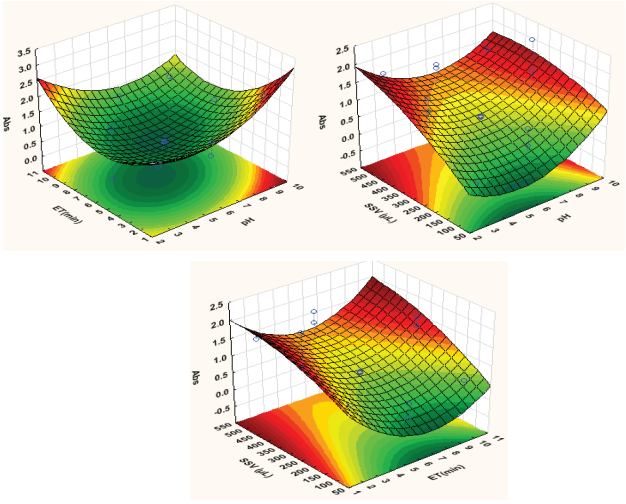

Figure 2: Response surfaces obtained for triclosan after extraction and preconcentration by supramolecular solvent extraction.

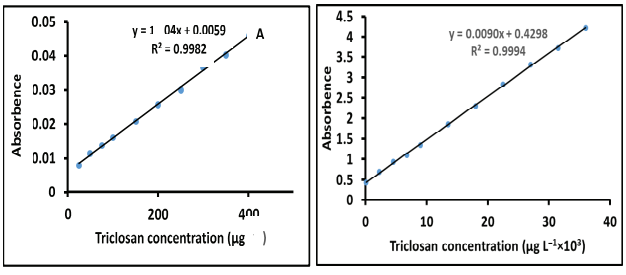

Figure 3: calibration curve for triclosan (A) before and (B) after preconcentration using VA-SSME .

(equation not included) were used to calculate the optimum conditions.

The 3D surface response plots were used to investigate the relationship/interaction between the independent variables (sample pH, extraction time and supramolecular solvent volume) on the absorbance of the samples. Based on quadratic expressions [33], the calculated optimum conditions for further processesing and application of the method were a pH of 5, extraction time of 6 minutes and supramolecular solvent volume of 400 µL. The confirmatory experiments were performed to validate the optimum conditions obtained by RSM and the results were not significantly different from the predicted values at 95% confidence level. These conditions were then used for the investigation of the analytical performance and validation and application of the procedure in real samples.

3.2 Analytical figures of merit

Under the determined optimum experimental conditions, the analytical performances of the developed SSME method for preconcentration and spectrophotometric determination of triclosan were investigated. The calibration curves (Figure 3) were obtained after a set of standard solutions (0 to 400 µg L^{-1}) was processed using the described extraction procedure. The concentrations of the analytes in the eluent solutions were quantified with the aid of a UV spectrophotometer. The limits of detection and quantification were calculated using the formulas: LOD = $\frac{3\times Sd}{b}$ and LOQ = $\frac{10\times Sd}{b}$, where *Sd* is the standard deviation of 10 replicate measurements of blank samples and *b* is the slope of each calibration curve. Dynamic linear ranges, correlation coefficient, enrichment factor, LOD and LOQ were determined to be LOQ-400 µg L^{-1}, 0.9994, 90, 0.28 µg L^{-1} and 0.92 µg L^{-1} respectively. The precision of the UA-SSME/UV procedure was evaluated as intra- (repeatability) and inter- (reproducibility) day precision, which were analyzed using six replicates (n = 15) for intra-day and eighteen replicates (n = 7) for inter-day. The results were expressed in terms of relative standard deviation (%RSD). Under optimum conditions, both intra-day and inter-day precisions were found to be 2.4% and 5.2%, respectively.

The performance of the developed VA-SSME/UV method for the preconcetration and determination of TCS in wastewater samples was compared with different published analytical procedures (Table 3). It can be seen that the current method has better performance in terms of LOD and LOQ when compared with those reported [34]. In addition, the developed method had a wider DLR compared to several published reports [34,35,37-41] and the % RSD was comparable with all the reported studies except one [37]. This optimal performance can be attributed to the fact that SUPRAS provide a number

Table 3: Comparison of analytical figures of merit for different extraction and detection methods for triclosan and other emerging pollutants.

Analyte	Matrix	Method	LOD (μgL^{-1})	LOQ (μgL^{-1})	DLR	RSD	References
Triclosan	Tapwater	SPME-LC-UV	0.001	0.033	0.01-168	7	[37]
Triclosan	Surface water	SPME-HPLC-UV	0.04	0.13			[38]
Triclosan	Urine	ULLME-HPLC-DAD	0.11	0.36	0.5-500	0.64-4.6	[36]
Triclosan	River water	SPME-HPLC-UV	0.00024	0.0008	0.0005-0.04	4	[39]
Triclosan	Cosmetics	IT-USA-SI-LLME-HPLC-UV	0.00009	0.0003	0.0004-0.1	0.8-5.3	[40]
Triclosan	Water, beverages and urine	DLLME-UV	4	13.3	0.02-2	-	[34]
Triclosan	Environmental water	SPE-GC	0.0001	0.0003	0.004-5	4.7-5.9	[41]
Triclosan	Aqueous samples	IT-USAEME-GC-μECD	0.004	0.013	0.02-2	2.8-5.4	[35]
Triclosan	Wastewater	SSME-UV	0.28	0.95	0.95-400	2.4-5.2	Current work

of possible interaction between the analyte and solvent including high number of binding sites and hydrogen bond interactions which increase the extraction efficiency [27]. However, the LOD and LOQ were higher than those reported by Refs [35-41].

SPME= Solid phase microextraction, LC-UV= Liquid chromatography-Ultraviolet detection, HPLC= High pressure liquid chromatography, ULLME= ultrasound-assisted liquid-liquid microextraction, DAD= Diode array detector, IT-USA-LLME= In-tube based ultrasound-assisted salt-induced liquid-liquid microextraction, DLLME= dispersive liquid-liquid microextraction, SPE= Solid phase extraction, GC- Gas chromatography, IT-USAEME= In-tube ultasonication-assisted emulsification microextraction, GC-μECD= Gas chromatography-micro-electron-capture detection, SSME= Supramolecular solvent microextraction

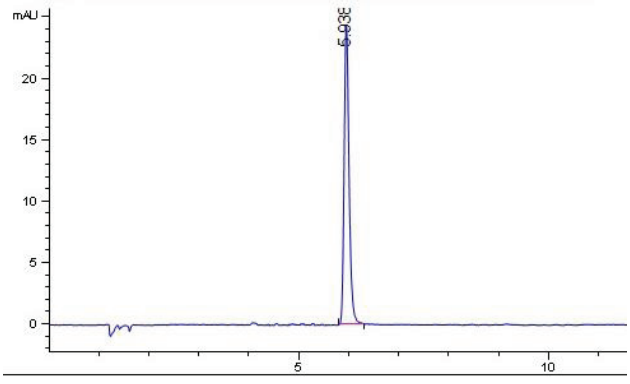

Figure 4: HPLC-PDA chromatogram for triclosan from influent sample spiked with 50 μg L^{-1} of the analyte after preconcentration using the VA-SSME.

3.3 Validation and Application

Due to the absence of reference material, the method was validated by the use of a spiked recovery test. The influent and effluent samples were spiked at two different concentrations as indicated in Table 4. The samples were then preconcentrated in triplicate using the proposed method as described in the experimental section prior to their analysis using a UV spectrophotometer and HPLC-PDA. It can be seen that the results obtained using the current method were comparable with those obtained using HPLC-PDA. In addition, the chromatogram (Figure 4) proved that, under optimum conditions, the developed method was able to extract triclosan from complex matrices.

The described method was applied in the determination of triclosan from wastewater samples collected over a period of 3 months: August, September and October of the same year (Table 5). It should be noted that the above concentrations were determined from influent samples. In the effluent samples, triclosan was not detected. The lack of detectable triclosan in effluent can be explained by the fact that the Daspoort waste water treatment has three types of treatment stages, including chlorinated and ultraviolet treatment before the effluent is released into the nearby river. This secondary treatment can possibly lead to either the degradation of triclosan or transformation into other compounds, as triclosan has been known to be able to be transformed into other compounds [6]. In summary, in the effluent the concentration of triclosan was below the limits of the method. The triclosan concentrations obtained using the developed method was confirmed by a reference method (HPLC-PDA). According to the student t-test, the results were not significantly difference at the 95% confidence level.

Table 4: Analysis of wastewater samples (influent and effluent) spiked and unspiked from Daspoort (Pretoria, Gauteng, South Africa) wastewater treatment plant.

Sample		SSME-UV-Vis		HPLC-PDA	
	Added (μgL^{-1})	Found (μgL^{-1})	% R	Found (μgL^{-1})	%R
Influent	0	10.01±0.5		9.93±1.3	
	50	59.07±0.8	98.12	59.88±3.7	99.90
	100	116.97±1.4	107.0	109.8±3.3	99.87
Effluent	0	nd		nd	
	50	50.16±0.9	100.31	49.89±2.5	99.78
	100	101.22±1.5	101.22	99.97±3.9	99.97

Table 5: Analysis of wastewater samples (influent and effluent) collected from Daspoort (Pretoria, Gauteng, South Africa) wastewater treatment plant over three months (concentration in $\mu g\ L^{-1}$, n = 4).

	Samples	VA-SSME/UV	HPLC-PDA
August	Influent	10.82± 0.5	11.01±1.6
	Effluent	nd	nd
September	Influent	10.67 ± 0.4	10.41±2.3
	Effluent	nd	nd
October	Influent	9.93 ± 0.34	10.11±3.1
	Effluent	nd	nd

4 Conclusions

In this study, a rapid and simple SSME/UV-Vis spectrophotometric method for preconcetration and determination of triclosan in wastewater samples was developed. The developed VA-SSME/UV method was solvent minimized, inexpensive, eco-friendly, precise and accurate. The analysis of wastewater samples revealed that the target analyte was present in all influent samples, while it was not detected in effluent samples. These findings suggested that triclosan was transformed to other compounds during the wastewater treatment process. Since even the reference method (HPLC-PDA) did not detect triclosan in the effluent samples, this demonstrated the effectiveness of the tertiary treatment stage.

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