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Microwave assisted extraction followed by gas chromatography with tandem mass spectrometry for the determination of triclosan and two related chlorophenols in sludge and sediments

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Abstract

A procedure for the determination of 2-(2,4-dichlorophenoxy)-5-chlorophenol (Triclosan) and two possible transformation compounds, 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP), in sludge from sewage treatment plants (STP) and sediments is presented. Extraction was performed using an acetone:methanol (1:1) mixture under the action of a microwave field. The centrifuged supernatant was diluted with a NaOH aqueous solution and twice extracted with *n*-hexane for removing neutral and basic interferences. The aqueous layer was acidified and processed as a waste water sample. After concentration analytes were silylated and determined by gas chromatography with tandem mass spectrometry (GC–MS/MS). Influence of experimental conditions on the yield of the extraction process and on the efficiency of the further clean-up step was thoroughly evaluated. Performance of MS/MS detection in comparison to single MS is described. Under final working conditions quantification limits between 0.4 and 0.8 ng/g and recoveries from 78% to 106% were obtained. The method was applied to the analysis of several sludge and sediment samples. Only low levels of TCS were detected in some of the sediments; however, all three compounds were found in sludge samples at concentrations ranging from 7 to 316 ng/g, in the case of chlorophenols, and from 420 to 5400 ng/g, for Triclosan.

Keywords: Triclosan; MAE; GC–MS/MS; Sludge; Sediment

1. Introduction

Triclosan (TCS), 2-(2,4-dichlorophenoxy)-5-chlorophenol, is extensively employed as an additive in many products because of its bactericide and antimicrobial properties [1,2]. Particularly, personal care products such as tooth pastes, mouth rinses, antiperspirants and hand soaps are the main responsible for direct discharges of this compound in domestic waste water [3,4]. Once in the aquatic environment, TCS can undergo a series of transformation reactions to produce, in some cases, more toxic and/or bio-accumulative compounds [5,6]. One of the fastest and most favourable is the oxidation of TCS by sodium hypochlorite, which is already present in tap water, or is introduced in waste water sewers by domestic disinfecting products. This reaction leads to the formation of relatively unstable tetra and pentachlorinated diphenyl ethers, which are further decomposed into dichloro and trichlorophenols [7,8]. Those reactions have been demonstrated in laboratory experiments; moreover, in previous articles, we have confirmed the simultaneous presence of TCS, 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) in sewage water samples [9,10].

In order to obtain a reliable estimation of the TCS removal in sewage treatment plants (STP), the concentration of the parent pollutant, and its transformation products, should be

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determined in both, the water phase and the solid sludge. The first aim can be achieved using solid-phase extraction or solid-phase microextraction followed by a chromatographic technique coupled to mass spectrometry [8,11,12]. Using these approaches it has been found that TCS levels in the outlet water stream of most STP represent only between 5% and 20% of those contained in the inlet of the same plants [13–15]. However, little information is available regarding the non degraded percentage of the compound remaining in the sludge. Considering the lipophilic behaviour of TCS ($\log K_{ow}$ 4.8) this percentage should not be negligible, as it has been confirmed in some recent works [15,16]. Knowing TCS levels in sludge is also important to establish the final uses of this bio-solid residue. Some common applications such as disposal in agriculture fields, or incineration may contribute to the re-introduction of the native pollutant in the biosphere and to the formation of polychlorinated dibenzo-*p*-dioxins [17], respectively.

Determination of TCS, and in general of any organic waste water pollutant, in sludge is a difficult task in comparison to its analysis in other solid matrices such as sediments. The high content of organic matter in sludge produces a diminution in the yield of the extraction step and, specially, makes necessary an exhaustive clean-up of the extract previously to obtain a chromatographic analysable solution [18]. From our knowledge, up to now, only Soxhlet [16], accelerated solvent extraction [15] and supercritical CO_2 [14] have been successfully applied to the extraction of TCS from sludge. In the first case interfering compounds were removed using normal phase sorbents and gel permeation chromatography [16], in the others only silica was used to retain very polar interferences [14,15]. Sample preparation procedures dealing with the simultaneous extraction of TCS and related chlorophenols from sludge samples have not been reported.

The aim of this work is to develop a procedure for the determination of TCS, 2,4-DCP and 2,4,6-TCP in sludge from urban STP and sediments. Microwave assisted extraction (MAE) was chosen as the extraction technique due to its capacity to process simultaneously several samples. Analytes were isolated from co-extracted compounds in function of their acid-base properties and polarity [19]. Influence of different factors on the yield of extraction and clean-up steps was systematically evaluated. Compounds were silylated and selectively determined by gas chromatography in combination with mass spectrometry. The need of MS/MS detection, instead single MS, is discussed in terms of achieved quantification limits and sample complexity.

2. Experimental

2.1. Reagents, standards and materials

Sodium hydroxide, formic acid, hydrochloric acid, HPLC grade methanol and acetone, *n*-hexane and ethyl acetate for trace analysis were obtained from Merck (Darmstadt, Germany). TCS, 2,4-DCP, 2,4,6-TCP and *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) were purchased from Aldrich (Milwaukee, WI, USA). Individual solutions of these compounds were prepared in acetone. Diluted standards and analyte mixtures were dissolved in both ethyl acetate (used as calibration standards) and acetone (used for spiking sediment and sludge samples). Calibration solutions were prepared by mixing 500 μl of standards in ethyl acetate, containing increasing concentrations of the analytes, with 50 μl of MTBSTFA. The silylation reaction was completed in 5 min at room temperature [10].

SPE cartridges containing 60 mg of the OASIS HLB polymer and normal phase silica cartridges (500 mg) were provided by Waters (Milford, MA, USA).

2.2. Samples

Spiked and non-spiked sludge and sediment samples were used in this study. Sludge samples were obtained from an urban STP equipped with primary and secondary (activated sludge) treatments. Disinfected sludge was also obtained from the same plant. Samples from two urban waste water plants were provided by the local water supplier company. River and marine sediments were collected in different points in the North West of Spain. All samples were kept at −18 °C until being lyophilised. After sieving, the fraction with a particle size below 300 μm was taken.

Optimization of sample preparation conditions was performed using a pool composed of an 80:20 mixture of primary and secondary sludge spiked with 2,4-DCP and 2,4,6-TCP. Recoveries of the proposed method were evaluated using aged samples of sediment, primary, biological and disinfected sludge spiked with the three analytes at different concentration levels.

2.3. Sample processing

Microwave assisted extractions were performed using an Ethos Microwave Extraction System (Milestone, Leutkirch, Germany), equipped with 12 pressurized 100 ml vessels. Under final conditions, samples (1 g for sediments, and 0.5 g in the case of sludge) were extracted using 30 ml of a 1:1 acetone: methanol mixture at 130 °C for 20 min. Extracts were centrifuged, the supernatant solution was mixed with 100 ml of NaOH 0.2 M and washed twice with 15 ml of *n*-hexane. The remaining aqueous phase was re-adjusted at pH 2.5 and concentrated on a 60 mg OASIS HLB SPE cartridge [10]. The extract from this sorbent was loaded on top of a silica cartridge. Analytes were recovered using 5 ml of ethyl acetate and this extract evaporated to 2 ml. Derivatization was performed using same conditions as for calibration standards.

2.4. Equipment

Analytes were determined by gas chromatography with tandem mass spectrometry (GC–MS/MS). The employed

Table 1
Retention times for derivatized analytes and MS/MS operation conditions

Compound	Retention time (min)	Parent ion (*m*/*z*)	Excitation storage level (*m*/*z*)	Excitation amplitude (V)	Product ions (*m*/*z*)
2,4-DCP	15.67	219	96	0.53	183[a], 147
2,4,6-TCP	17.26	255	110	1.10	217[a],235, 183
TCS	23.04	347	140	1.50	200[a], 310[a], 219

[a] Used as quantification ions.

system consist of a Varian CP 3900 Gas Chromatograph (Walnut Creek, CA, USA) connected to an ion-trap mass spectrometer (Varian Saturn 2100). Separations were carried out using a HP-5 MS capillary column (30 m × 0.25 mm i.d., d.f.: 0.25 um) supplied by Agilent (Wilmintong, DE, USA). Helium (99.999%) was used as carrier gas at a constant flow of 1 ml/min. The injected volume was 1 μl in splitless mode (purge time 2 min). The GC oven was programmed as follows: 2 min at 50 °C, at 10 °C/min to 270 °C (held for 10 min). The GC–MS interface and the ion trap temperatures were set at 270 and 220 °C, respectively. Mass spectra were obtained in the electron impact (EI) mode (70 eV) in the range from 100 to 550 *m*/*z*. The parent ion cluster for each silylated analyte, corresponding to the loss of the *tert*-butyl group [M − 57], was isolated with a *m*/*z* window of ±3 units and submitted to collision induced dissociation. Working MS/MS conditions, as well as *m*/*z* ratios for parent and product ions are given in Table 1.

Concentrations of the analytes in sediment and sludge extracts were determined using external calibration. Unless otherwise is stated, MS/MS detection was employed as quantification technique.

3. Results and discussion

3.1. Performance of GC–MS/MS analysis

Performance of GC–MS/MS detection was evaluated using silylated standards in ethyl acetate. Linearity was tested in the concentration range from 1 to 1500 ng/ml, by injecting standards at seven different concentration levels. Correlation coefficients between 0.996 and 0.999 were obtained, Table 2. Relative standard deviations for five consecutive injections of standard solutions at different concentration levels ranged from 3.6% to 8.3%. Instrumental quantification limits of 0.2 ng/ml, 10 folds lower than those obtained using single GC–MS detection, were achieved, Table 2.

3.2. Preliminary experiments

Ethyl acetate, methanol and acetone were initially considered to recover the analytes from a spot spiked sludge sample. Those solvents were selected considering published articles dealing with the extraction of TCS or pharmaceutical compounds from sediments and sludge [16,20]. Extractions were performed at 110 °C for 20 min. In the three cases colourful, dark solutions, even after a clean-up step using a 500 mg silica cartridge, were obtained. This fact prevented their injection in the GC column and pointed the importance of developing a more effective clean-up approach for sludge samples.

3.3. Clean-up strategy

Species involved in this study are acidic compounds (pK_a values from 6.6 to 8.1). Therefore, they can be isolated from neutral and basic interferences, contained in sample extracts, by re-extraction into an aqueous solution at basic pH. The aqueous/organic distribution ratios of the analytes were investigated using water samples adjusted at two different pH values (11.5 and 13) with NaOH. Ethyl acetate and *n*-hexane were considered as organic solvents. Spiked Milli-Q water samples, aliquots of 100 ml, adjusted at the above pHs were twice extracted with 15 ml of *n*-hexane or ethyl acetate. The upper organic layer was discarded and the aqueous one acidified at pH 2.5 and concentrated using an OASIS HLB cartridge. After elution, analytes were silylated and determined by GC–MS. Responses (peak areas) were compared with those corresponding to aliquots of the same solution directly passed through the SPE sorbent, without a previous liquid–liquid partition step. Considering *n*-hexane as extraction solvent, analytes remained quantitatively in the aqueous phase, when it had been adjusted to pH 13. Using ethyl acetate, regardless of the aqueous phase pH, more than 50% of the initial concentration partitioned into the organic phase.

Table 2
Linearity, repeatability ($n = 5$ injections) and quantification limits of the detection method

Compound	Correlation coefficient (*r*)	Repeatability RSD (%)		QL (S/N 10), ng/ml	
		5 ng/ml	250 ng/ml	MS–MS detection	MS detection
2,4-DCP	0.997	4.2	4.1	0.2	4
2,4,6-TCP	0.996	4.4	3.6	0.2	4
TCS	0.999	8.3	5.3	0.2	2

Distribution of the analytes between the aqueous phase, at pH 13, and *n*-hexane were re-evaluated in presence of 30 ml of acetone or methanol. In both cases, none of the three analytes passed in a significant extension to the *n*-hexane layer. Moreover, after re-adjusting the aqueous layer at pH 2.5, the presence of methanol or acetone did not affect to the retention of the compounds in the SPE sorbent. In view of these results, in further experiments, methanol and acetone were considered as extraction solvents; whereas, ethyl acetate was only employed to elute the analytes from the SPE cartridge.

The above described clean-up procedure was applied to the microwave extract obtained from a sludge sample (0.5 g) spiked with 2,4-DCP and 2,4,6-TCP. This sample was extracted at 110 °C for 20 min, using 20 ml of methanol. After dilution with 100 ml of NaOH 0.2 M, the dark raw extract was washed with *n*-hexane. The emulsion between both phases was broken by the addition of sodium chloride (ca. 500 mg). The result was a transparent and practically colourless aqueous solution. It was adjusted at pH 2.5, concentrated on SPE cartridge and further purified over silica to eliminate very polar compounds not removed by *n*-hexane washing. Fig. 1 depicts the obtained GC–MS/MS chromatogram. Well defined peaks can be observed at the retention times of the three analytes, including TCS which had not been added to the sample. MS/MS spectra for these peaks matched with those corresponding to silylated standards of the analytes, figure not shown.

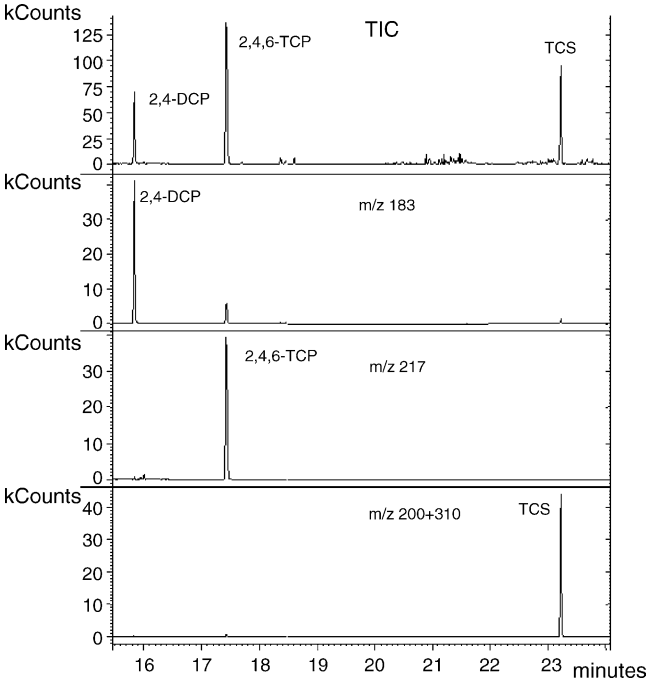

Fig. 1. GC–MS/MS chromatograms for a pooled sludge sample spiked only with 2,4-DCP and 2,4,6-TCP at the 2 μg/g level.

3.4. Optimisation of microwave extraction conditions

The effects of different parameters on the yield of the microwave extraction were evaluated using experimental factorial designs. Experiments were carried out using 0.5 g subsamples from a pooled sludge with an aged spike of 2,4-DCP and 2,4,6-TCP (2 μg/g). Microwave extracts were submitted to the above-mentioned clean-up procedure. In a first screening stage the influence of extraction temperature, solvent type, solvent volume and magnetic stirring on the yield of extraction process was evaluated using a two-level fractional factorial 2^{4-1} design in eight experiments. Low and high levels for the considered variables, together with the estimated values of their main effects are given in Table 3. The higher the absolute value for a main effect the larger the influence of the corresponding variable in the yield of the extraction. A positive sign indicates an improvement of the extraction efficiency when the factor changes from the low to the high level. Obviously, a negative sign indicates the opposite behaviour. In order to obtain enough degrees of freedom to calculate the statistical significance of those main effects, the less important factor for each compound was excluded from the design. Calculated standardized main effects for the remaining variables are also shown in Table 3.

The most important factor, and the only significant one at the 95% confidence level, was the extraction solvent. In the case of TCS and 2,4,6-TCP the efficiency of the extraction was higher using acetone, whereas for 2,4-DCP a better yield was achieved with methanol. Extraction temperature played a positive but non significant effect for all compounds. The magnitude and the sign of the main effect associated to the solvent volume was compound dependent: in the case of TCS showed a positive an relatively important effect, whereas, for 2,4-DCP the influence of solvent volume was negative and completely negligible. For all compounds, stirring played a

Table 3
Experimental domain and values of main effects associated to each factor considered in the fractional factorial (2^{4-1}) design

Factor	Low level	High level	Main effects values with their sign		
			2,4-DCP	2,4,6-TCP	TCS
Solvent	Acetone	Methanol	528 (32.4[a])	−164 (−6.0)	−1164 (−32.3[a])
Volume (ml)	15	30	−16	−40 (−1.5)	285 (7.9)
Temperature (°C)	90	130	50 (3.1)	60 (2.2)	192 (5.3)
Stirring	No	Yes	43 (2.6)	−27	−36

Data in brackets correspond to standardized main effects after removing the less important factor for each analyte.
[a] Significant factors at the 95% confidence level.

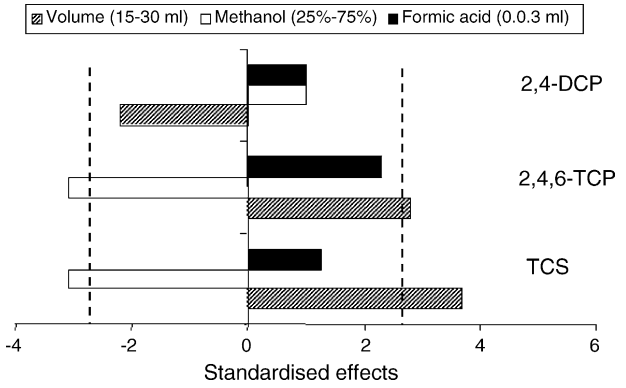

Fig. 2. Pareto graph showing the standardized main effects of factors included in the second factorial design. Low and high levels of each factor are given in the title of the figure. Dotted vertical lines represent the statistical significant bound.

very minor effect on the process. In view of those results, temperature was fixed at 130 °C and sample stirring was not considered in further extraction experiments.

A second two levels full factorial design, with one central point, was used to investigate in more detail the effects of solvent volume and composition. The addition of formic acid to the sludge was the third factor. Considering the pK_a values of the analytes their extraction efficiency could be enhanced in acidic media, particularly for sludge samples stabilized by addition of calcium carbonate. Low and high values for the 3 factors were 15–30 ml (solvent volume), 25%–75% of methanol (in the acetone:methanol extraction mixture) and 0–300 μl (formic acid). Standardized main effects obtained for each factor, after removing non-significant interactions, are depicted in Fig. 2. Vertical dotted lines in the graph represent the statistically significant bound at the 95% confidence level. The presence of formic acid improved the yield of the process, but without being statistically significant. The highest effect of this factor was observed for 2,4,6-TCP, which is the compound with the lowest pK_a value. In agreement with the behaviour observed in the first design, increased percentages of methanol in the extraction solution produced a significant diminution in the responses of TCS and 2,4,6-TCP. For 2,4-DCP the opposite pattern was observed; although, without being statistically significant. TCS and 2,4,6-TCP are more lipophilic species (log K_{ow} 4.8 and 3.6, respectively) than 2,4-DCP (log K_{ow} 2.9); therefore, the lower the polarity of the extraction solvent mixture the higher their extraction yield. The effect of solvent volume was also different for TCS and 2,4,6-TCP than for 2,4-DCP. For the two first compounds, it showed a positive and significant influence on the extraction process. For 2,4-DCP, it showed a non significant but negative effect. As the aim of this work was the simultaneous determination of the three pollutants, 30 ml of a 1:1 acetone:methanol mixture, containing 300 μl of formic acid, was used as extraction solution.

3.5. Performance of the method

Recoveries of the whole method, extraction plus clean-up, were evaluated using aged spiked samples corresponding to primary, biological and disinfected sludge, as well as river sediment. The percentage of organic carbon in those samples ranged from 0.8%, for the river sediment, up to 38% for primary sludge. Chlorophenols were added to samples at different concentration levels from 10 to 300 ng/g. TCS was spiked at two levels, 10 and 300 ng/g in the case of sediments, and at 0.9 and 5 μg/g to sludge samples. Non-spiked samples of the four materials ($n = 3$) were also processed. Recoveries were calculated by dividing the difference between the measured concentrations for spiked and non spiked samples by the added one. Obtained values ranged from 78.3% to 106.6%, with relative standard deviations below 13%, Table 4. These values can be considered as acceptable taking into account the complexity of the matrix and the number of steps involved in the sample preparation.

Quantification limits of the method, defined for a signal to noise ratio of 10 (S/N 10), ranged from 0.8 ng/g for sludge to 0.4 ng/g for sediments. These values are one order of magnitude lower than those previously reported for TCS with electron impact GC–MS detection [14,16] and in the same range of those achieved using GC–MS with negative chemical ionisation for sediments [21].

Advantages of using MS/MS detection, when compared to single MS, are not only related to a diminution in the quantification limits. Fig. 3 shows MS spectra for a peak appearing at the retention time of TCS in sediment and primary sludge spiked samples. The MS spectrum for this peak in the sediment (TCS spiked concentration 300 ng/g) matched with that corresponding to a silylated standard. However, for the sludge

Table 4
Recoveries for aged spiked samples, $n = 4$ replicates

Sample	% of organic carbon	Addition level (ng/g)	Recoveries ± RSD (%)		
			2,4-DCP	2,4,6-TCP	TCS
River sediment	0.8	10	81.8 ± 5.7	96.0 ± 4.9	98.7 ± 8.5
River sediment	0.8	300	79.1 ± 8.2	92.0 ± 8.9	99.7 ± 6.5
Primary sludge	38	300[a]	79.1 ± 8.2	98.9 ± 3.2	81.7 ± 6.5
Secondary sludge	36	300[a]	78.3 ± 8.1	87.6 ± 5.1	94.0 ± 6.5
Disinfected sludge	11	300[a]	106.6 ± 7.5	88.3 ± 5.0	82.2 ± 11.5
Disinfected sludge	11	40[b]	82.9 ± 9.2	97.4 ± 13.0	97.3 ± 10.5

[a] 5 μg/g for TCS.
[b] 0.9 μg/g for TCS.

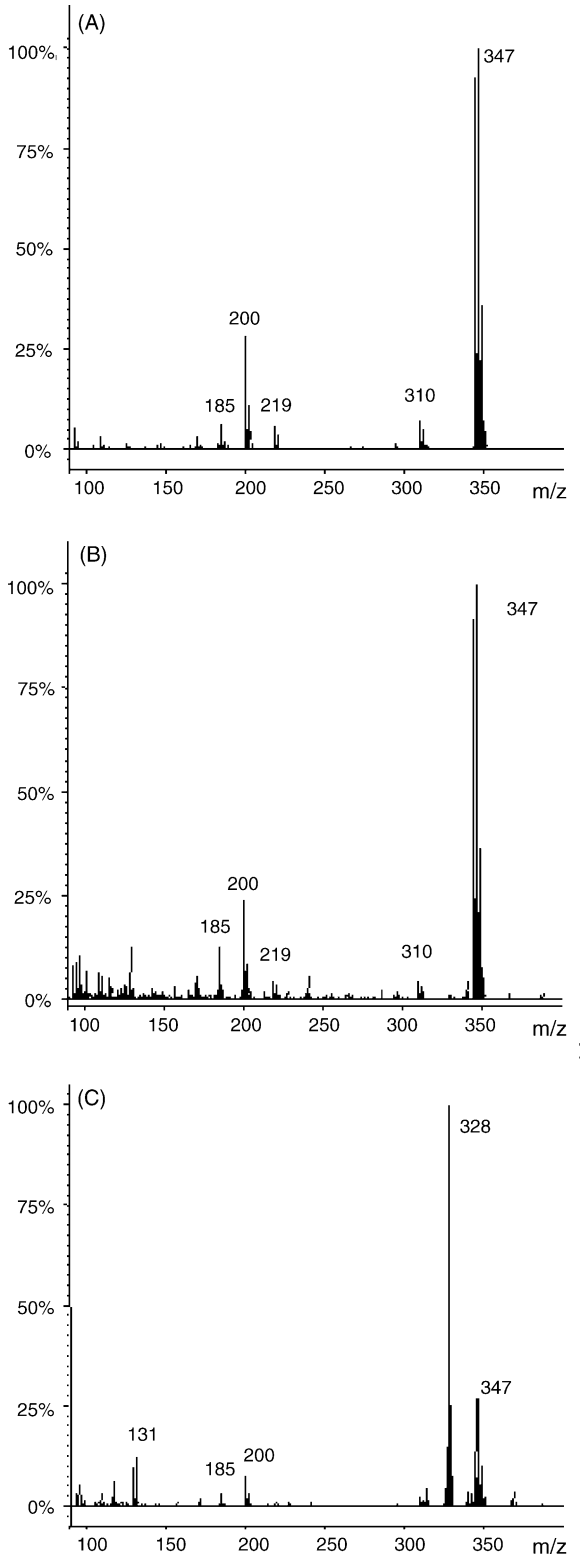

Fig. 3. MS spectra for the chromatographic peak at the TCS retention time in different samples. (A) Standard in ethyl acetate, 100 ng/ml; (B) spiked river sediment, 300 ng/g; (C) spiked primary sludge, 5000 ng/g.

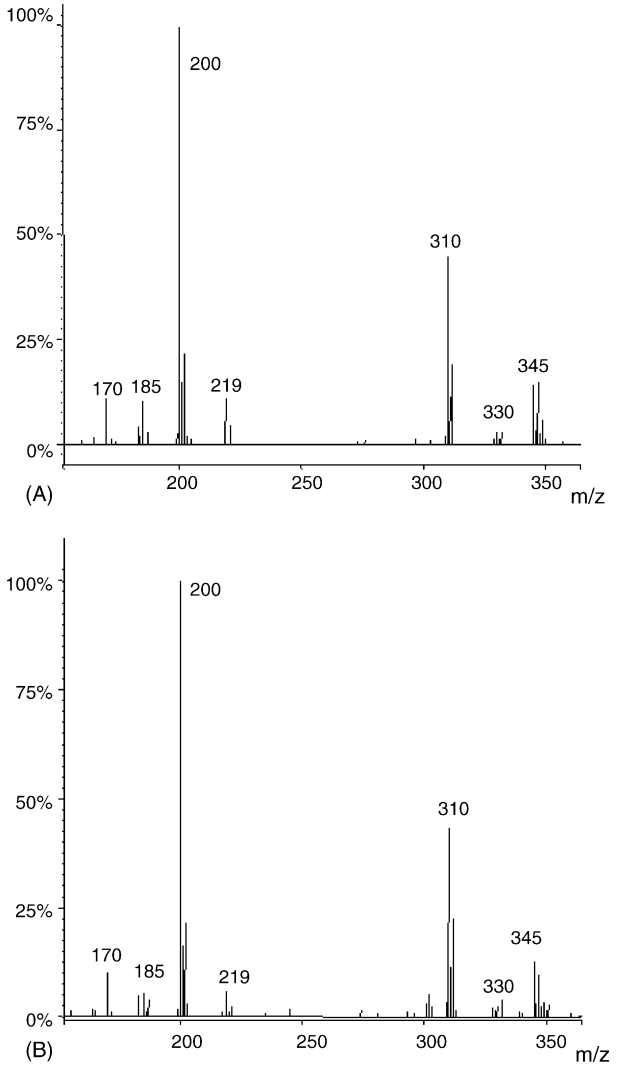

Fig. 4. Comparison of MS/MS spectra for the peak at the retention time of TCS. (A) Standard in ethyl acetate, 100 ng/ml; (B) spiked primary sludge, 5000 ng/g.

sample (TCS spiked concentration 5000 ng/g), the spectrum contained an intense signal at *m/z* 328, corresponding to a coeluting interference. This fact makes difficult the identification of TCS in sludge using single MS detection, especially in samples polluted with the analyte at lower concentration levels. Fig. 4, compares MS/MS spectra for the same sludge extract and for a TCS standard. An excellent concordance was observed between both spectra.

3.6. Application to real samples

The proposed method was applied to the analysis of several grab samples corresponding to different sediments and sludge from urban STP. Regarding sediments, any of both chlorophenols was detected; whilst, TCS was measured in two of them at concentrations of 4 and 36 ng/g, Table 5. These values are similar to those found in Swiss lakes and

Table 5
Concentrations (ng/g) of the analytes in non-spiked sediment and sludge samples

Code	Sample type	Mean ± SD		
		2,4-DCP	2,4,6-TCP	TCS
1	River sediment	n.d.	n.d.	4.4 ± 0.8
2	River sediment	n.d.	n.d.	n.d.
3	River sediment	n.d.	n.d.	35.7 ± 1.1
4	Marine sediment	n.d.	n.d.	n.d.
5	Primary sludge	79.9 ± 8.5	19.4 ± 0.3	2543 ± 50
5	Primary sludge[a]	89.8 ± 8.4	21.6 ± 1.5	2696 ± 270
6	Biological sludge	316 ± 33	38.1 ± 9.2	5400 ± 125
6	Biological sludge[a]	349 ± 12	37.7 ± 2.5	5388 ± 316
7	Disinfected sludge	77.9 ± 8.5	15.8 ± 2.4	1508 ± 196
8	Sludge	74.4 ± 1.0	7.5 ± 1.0	1474 ± 240
9	Sludge	55.2 ± 3.3	14.5 ± 0.5	418 ± 38

$N = 3$ replicates; n.d. under 0.4 ng/g.
[a] Soxhlet extraction.

marine sediments from the south of Spain [15,21]. Regarding sludge, all compounds were detected at concentrations from the low ng/g, in case of 2,4,6-TCP, up to 5.4 μg/g for TCS, Table 5. Accuracy of those values was evaluated by extracting two of the sludge samples with 100 ml of acetone: methanol (1:1) for 24 h using the Soxhlet technique. Results were in an acceptable agreement with those obtained with the developed method. Samples 5, 6 and 7 correspond to the same sewage plant. Even considering that the highest concentrations were found in the biological sludge, the most environmental relevant finding is the presence of the investigated species in the disinfected sludge. This residue is a mixture of dewatered sludge (primary and secondary) and calcium carbonate. Normally, it is employed as a fertilizer in agriculture. This use contributes to the spread and reintroduction of the analytes in the environment. Samples 8 and 9 also correspond to urban STP; although, no information was available regarding employed waste water treatments. Globally, the levels of TCS found in the processed sludge samples are within the range of concentrations reported for different plants in Germany [16] and in the United States [14].

4. Conclusions

A procedure for the determination of TCS and two chlorophenols in sludge and sediment samples has been proposed. Solvent composition and volume are the most significant parameters from the point of view of the microwave assisted extraction efficiency. Sludge samples required an exhaustive clean-up to remove co-extracted compounds; moreover, MS–MS detection is recommended to improve the reliability of determinations for these samples. The whole procedure showed suitable recoveries and sensitivity for the analysis of sediments and sludge from urban sewage treatment plants. Further improvements should be focussed on shortening the clean-up step without decreasing its efficiency.

Preliminary data, from a reduced number of sludge samples, confirmed the presence of the target species over the quantification limits of the method. Levels of 2,4-DCP and 2,4,6-TCP are lower than those corresponding to TCS; however, their higher persistence and endocrine disrupter properties should be taken into account in order to determine the destination of those solid wastes.

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