

Determination of Triclocarban, Triclosan and Methyl-Triclosan in Environmental Water by Silicon Dioxide/Polystyrene Composite Microspheres Solid-Phase Extraction Combined with HPLC-ESI-MS

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This paper developed a sensitive and efficient analytical method for triclocarban (TCC), triclosan (TCS) and Methyl-triclosan (MTCS) determination in environmental water, which involves enrichment by using silicon dioxide/polystyrene composite microspheres solid-phase extraction and detection with HPLC-ESI-MS. The influence of several operational parameters, including the eluant and its volume, the flow rate and acidity of water sample were investigated and optimized. Under the optimum conditions, the limits of detection were 1.0 ng/L, 2.5 and 4.5 ng/L for TCC, TCS, and MTCS, respectively. The linearity of the method was observed in the range of 5 - 2000 ng/L, with correlation coefficients (r^2) > .99. The spiked recoveries of TCC, TCS and MTCS in water samples were achieved in the range of 89.5% - 96.8% with RSD below 5.7%. The proposed method has been successfully applied to analyze real water samples and satisfactory results were achieved.

Keywords: Triclocarban; Triclosan; Solid-Phase Extraction; Silicon Dioxide/Polystyrene Composite Microspheres; HPLC-ESI-MS/MS

Introduction

Over the past decades, increasing residues of pharmaceuticals and personal care products (PPCPs) have been detected in the aquatic environment. Hundreds of tones of these compounds are dispensed in communities every year. The continuous input of such compounds may affect water quality and potentially affect the ecosystem and human health (Halden & Paull, 2005; Ahn et al., 2008; Chalew & Halden, 2009). Triclocarban (N-(4-chlorophenyl)-N-(3,4-dichlorophenyl)urea, TCC) and triclosan (5-chloro-2-(2,4-dichloro-phenoxy)-phenol, TCS) are both antimicrobials that are added to a wide range of household and personal-care products, such as shampoos, soaps, creams, mouthwash and toothpaste. However, TCC has harmful effects on humans and other animals because it increases methemoglobinemia (Ponte et al., 1974). TCC exposure enhances the estradiol-dependent or testosterone-dependent activation of the estrogen receptor-responsive and the androgen receptor-responsive gene expression in human ovary cells (Ahn et al., 2008). Moreover, TCC affects the transcription of genes that respond to the thyroid hormone in frog and rat cells (Hinther et al., 2011). Bioaccumulation studies have shown that TCC accumulates in algae (Coogan et al., 2007) and snails (Coogan et al., 2008). Similarly, TCS was found to be acutely toxic to a number of aquatic organisms, particularly for algae species, and was recently shown to modulate thyroid function of amphibians at concentrations as low as .15 µg/L (Orvos et al., 2002).

In addition, triclosan has been shown to phototransform into chlorinated dibenzodioxins (Mezcua et al., 2004). Methyl-triclosan (MTCS) is a metabolite of TCS. It is more lipophilic and environmentally persistent (Chu & Metcalfe, 2007; Coogan et al., 2007), suggesting its relatively high bioaccumulation potential in aquatic organisms (Coogan et al., 2007).

The potential risk to the environment and human health generated by TCC, TCS and MTCS is currently drawing considerable attention worldwide. Therefore, it is very essential to establish simple, sensitive and reliable analytical method to determine these compounds in various environmental water samples for safety evaluation.

Generally, a sample enrichment and clean-up procedure are often needed prior to the instrumental determination because these pollutants are present at very low levels in environmental water samples (µg/L or less). Many sample pretreatment methods, such as liquid-liquid extraction (LLE) (Canosa et al., 2007; Sun et al., 2012), dispersive liquid-liquid microextraction (DLLME) (Guo et al., 2009; Zhao et al., 2011), solid-phase extraction (SPE) (Halden & Paull, 2004; Sapkota et al., 2007), solid-phase micro-extraction (SPME) (Montes et al., 2005), hollow fiber assisted liquid-phase microextraction (HF-LPME) (Zhao et al., 2007), and stir bar sorptive extraction (SBSE) (Kawaguchi et al., 2008) have been used for the enrichment of TCS and TCC.

Traditional LLE is widely used as a sample preparation technique by several authors (Liska et al., 1989), but it is tedious, time consuming, costly and needs large volumes toxic and

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flammable solvents. SPME has drawbacks of high cost, sample carry-over, and a decline in performance with time. LPME produces some obvious disadvantages: solvent drops are ready to break, air bubble is tending to form, time is long and sometimes equilibrium is not achieved easily in short time (Melwan-ki & Fuh, 2008).

SPE has distinguished from many extraction techniques and has been widely used for the concentration and measurement of many pollutants (Halden & Paull, 2004; Chu & Metcalfe, 2007; Sapkota et al., 2007). SPE has been an effective sample-handling technique with many obvious advantages such as high recovery, high pre-concentration factors, low consumption of organic solvents, simplicity, easy operation and automation. In SPE the analytes to be extracted are partitioned between a solid and liquid and these analytes must have a greater affinity for the solid phase than for the same matrix, which are better than the two immiscible liquids as in LLE. The different mechanisms of retention or elution are due to inter-molecular forces between the analytes, the active sites on the surface of the adsorbent and liquid phase or matrix. Therefore, the types of the adsorbents are the key to SPE process.

The silicon dioxide/polystyrene composite microspheres (SiO_2/PS) is a mixed-mode sorbent which was prepared through polymerization of styrene on the surface of SiO_2 . It has both a hydrophilicity of SiO_2 and a lipophilicity of polystyrene, and was successfully used to extract nitrophenol and alkylphenol from aqueous environmental samples (Shen S. C. et al., 2012).

Sensitive and selective approaches for determination of TCC, TCS and MTCS have been established, including GC/MS (Coogan et al., 2007; Kawaguchi et al., 2008), GC/MS/MS (Boehmer et al., 2004), LC/MS (Chu & Metcalfe, 2007; Sapkota et al., 2007) and LC/MS/MS (Zhao et al., 2011; Shen J. et al., 2012). In order to reduce complex derivatization step and possible interferences of other compounds, HPLC-ESI-MS was selected for the sensitive determination of TCC, TCS and MTCS because they are compounds with strong polarity.

The aim of this work is to develop a rapid SPE-UHPLC-MS method for simultaneous determination of TCC, TCS and MTCS in environmental water samples. To accomplish its application in environmental monitoring of environmental water, silicon dioxide/polystyrene (SiO_2/PS) SPE cartridges was selected for the pre-concentrations. A series of key parameters influencing the enrichment efficiency of TCC, TCS and MTCS have been investigated and optimized. It could provide enough valid evidence for post-study.

Materials and Methods

Materials

HPLC-grade methanol, acetonitrile, and acetone were purchased from Tedia Company Inc. (Fairfield, Ohio, USA). TCC were purchased from Dajie Technical Co. Ltd. (Hunan, China). TCS and MTCS were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Standard stock solution of TCC, TCS and MTCS (100 mg·L) was prepared in methanol and then stored at 4°C. Fresh working solutions were prepared daily by diluting the stock solution with purified water. The SiO_2/PS sorbent (5 μm) was obtained from Lantian Pharmaceutical co. Ltd. (Wuhan, China).

A SiO_2/PS packed cartridge was prepared by modifying an Agilent cleanert ODS C_{18} cartridge (70 mm \times 14 mm, 6 mL, polypropylene), which was purchased from Agilent Techno-

logies (Palo Alto, CA, USA). 500 mg of SiO_2/PS sorbent was packed into the cartridge, after the C_{18} packing was evacuated. The polypropylene upper frit and lower frit were placed at each end of the cartridge to hold the SiO_2/PS packing fixed. Then the bottom end of the cartridge was connected to a SHBIII vacuum pump (Great Wall Scientific and Trade Co. Ltd., Zhengzhou, Henan), and the upper end of cartridge was connected with a PTFE suction tube, the other end of which was immersed into the water sample. The whole SPE device was washed by sufficient methanol and purified water before the first usage, in order to avoid the pollution of organic contaminants.

Instruments

The high-performance liquid chromatography-mass spectrometry equipment was an Agilent 1100 LC system, including an electrospray ionization mass spectrometer (ESI-MS), a quaternary pump, a column thermostat, and an automatic sample injector with a 100 μL loop. A personal computer equipped with the Agilent ChemStation program for HPLC-MS was used to process the chromatographic data. An Agilent Eclipse XDB- C_8 column, 4.6 mm \times 150 mm, 5 μm particle size, was used to held at 30°C to analyze TCS. The injected sample volume was 10 μL , and the binary mobile phase was composed of 25% water and 75% methanol (v/v) at a constant flow rate of .8 mL/min. Under these chromatographic conditions, one HPLC-MS run can be finished within 10 min. MS conditions were maintained as follows: drying gas 10.0 L/min; nebulizer pressure 30 psi; chemcur. .32 μA ; quadratic temperature 99°C; high vac. 1.1×10^{-5} Torr. Target compounds analysis was carried out in negative ionization mode and quantification was performed under SIM conditions.

SPE Procedure

The cartridge packed with SiO_2/PS adsorbent was conditioned with 10 mL of methanol in acetone (50%), followed by 5 mL of methanol and 5 mL of water before use. Aliquots (300 mL) of water sample were passed through the cartridges at a flow rate of approximately 10 mL/min. Following the loading of the sample, the cartridge was eluted with 5 mL hexane, and 5 mL dichloromethane to remove the co-adsorbed matrix substance. After the cartridge was dried with a vacuum, 2 \times 5 mL of 5% methanol in water was used to wash it. Then the cartridge was dried under vacuum for 10 min. The cartridge was eluted with 3 \times 5 mL methanol in acetone (50%) at a slow rate of 1 mL/min. The combined extract was dried under N_2 gas and then reconstituted in .5 mL of methanol.

Results and Discussion

Method Development

Selection of the Adsorbents

SPE has gained popularity as a technique for the extraction of polar to medium-polarity analytes from aqueous environmental samples. With a number of different sorbents applied in SPE and all kinds of commercial SPE cartridges emerged in the market, SPE can almost meet all the demands of preconcentrations and clean-up in the environmental monitoring. The recoveries of TCC, TCS and MTCS were investigated by using four different SPE cartridges: Agilent SampliQ Optimised Polymer technology (OPT), Agela Cleanert PEP, bamboo-activated char-

coal (BAC) and SiO₂/PS with eluate of 50% methanol in acetone. As shown in **Figure 1**, the experimental results indicate that the OPT sorbent is unsuitable for the isolation of TCC, TCS and MTCS because of its poor recoveries. The Agela Cleanert PEP and the BAC sorbents showed efficient selective adsorption for TCC, TCS and MTCS, respectively. However, these SPE cartridges are unsuitable for the simultaneous determination of all three analytes. Only the SiO₂/PS sorbent showed satisfactory recoveries for TCC, TCS and MTCS and was thus selected to be the SPE material in this study.

Selection of the Eluant and Its Volume

Eluant is a key parameter that affects the recovery of target compounds. Three eluants, including methanol, acetone, and 50% methanol in acetone, were tested. The results indicate that 50% methanol in acetone has better desorption efficiencies (the recoveries were 91.2%, 94.5% and 96.0% for TCC, TCS and MTCS, respectively), as shown in **Figure 2**. Therefore, 50% methanol in acetone was chosen as the eluant.

Then the effect of eluant volume which directly affects the recovery of analytes was investigated. A series of experiments were designed and performed by changing the volumes of eluant over the range of 2.3 - 15.0 mL. The results showed that the recoveries TCC, TCS and MTCS increased with the increase of the eluant volume between 3.0 mL and 9.0 mL (**Figure 3**). When the volume is more than 9.0 mL, the extraction efficiencies of TCC, TCS and MTCS almost kept constant. Therefore, 9.0 mL eluant was used as the eluant in all subsequent experiments.

Influence of pH

To examine the effect of the pH of the water sample on the

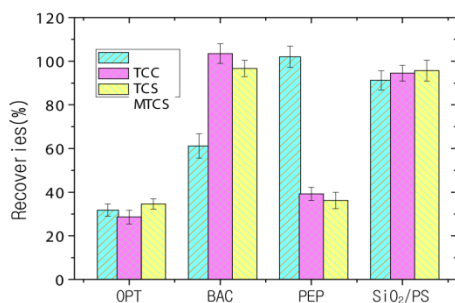


Figure 1. Effect of adsorbents on the recoveries of TCC, TCS and MTCS.

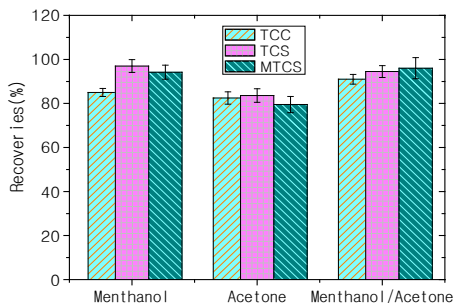


Figure 2. Effect of eluant on the recoveries of TCC, TCS and MTCS.

recoveries of TCC, TCS and MTCS, a series of experiments were performed by changing the pH of the water samples from 2.0 to 13.0, as shown in **Figure 4**. The result indicates that the recoveries of TCC, TCS and MTCS maintain high from pH 2 to pH 10. However, under the condition of alkalinity, the recovery of TCC kept satisfactory while that of TCS and MTCS dropped dramatically. This result may possibly be attributed to the structural characteristics of TCS. Strong alkalinity may result in the deprotonation of the hydroxyl of TCS and MTCS, which affects their solubility in water. According to these experimental results, the pH of solutions was adjusted in the range from 4.0 to 6.0 in the subsequent experiments.

Influence of Flow Rate

The flow rate of water sample affects the recovery of TCS and controls the sample pretreatment time. Here, the flow rates of the sample were optimized in the range of 1.0 - 3.0 mL/min with the limitation on the negative pressure of the pump. The results from **Figure 5** show that the flow rate had no obvious influence on the extraction efficiency of TCC, TCS and MTCS. In order to save extraction time, the highest flow rate, 3.0 mL/min, was adopted in the following experiments

Method Validation

Under the given optimal conditions, a number of important parameters of the method, such as linearity range, correlation coefficient (r^2), reproducibility, limit of detection, and recovery, were studied. Linearity was tested by varying the concentrations of TCC, TCS and MTCS from 5 ng/L to 20,000 ng/L,

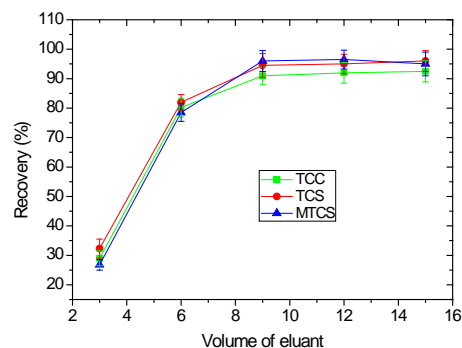


Figure 3. Effect of volume of eluant on the recoveries of TCC, TCS and MTCS.

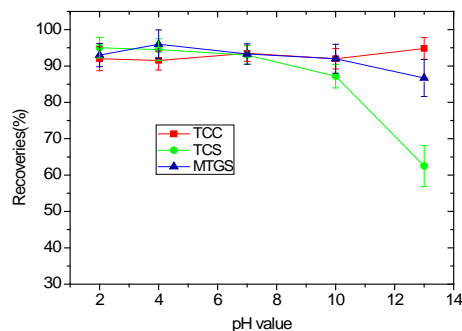


Figure 4. Effect of pH of samples on the recoveries of TCC, TCS and MTCS.

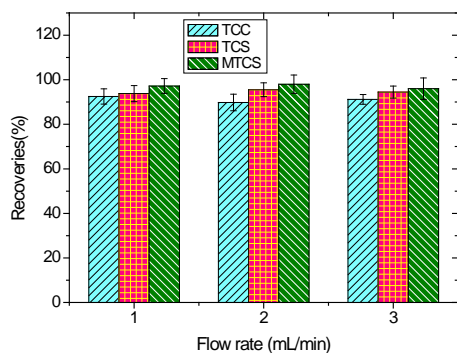


Figure 5.
Effect of flow rate on the recoveries of TCC, TCS and MTCS.

with $r^2 > .99$. Limits of detection (LOD) of the analytes were calculated with signal/noise ratios (S/N) of 3. Limits of quantification (LQD) were calculated with signal/noise ratios (S/N) of 10. Detailed information on the limits of the analytes was provided in **Table 1**.

To investigate the effects of the sample matrix, two water samples collected from Xiaoqing River were spiked with TCC, TCS and MTCS at different levels and were then analyzed. The recoveries of spiked water are listed in **Table 2**. The effects of the matrix on the signal were insignificant after sample clean-up by using SPE.

Determination of TCC, TCS and MTCS in Environmental Water Samples

For a preliminary survey and for method validation, the method developed was used for simultaneous analysis of the three target compounds in a variety of environmental water samples. Three river water samples were collected in Xiaoqing Rivers in Jinan area, Shandong Province, China. The sample 1# was collected in the upstream of the wastewater treatment plant, .5 km from the discharge port. The sample 2# was collected in the downstream of wastewater treatment plant near the discharge port, and samples 3# was collected downstream of wastewater treatment plant, apart from the discharge port 2 km. Two sea water samples collected in Yellow Sea at Qingdao port. Sample 1# was from the coast, and sample 2# was 2 km apart from the coast. **Figure 6** shows a typical HPLC-ESI-MS chromatogram obtained from a river water extract. The average concentrations of the target compounds in a variety of environmental water samples are listed in **Table 3**.

Conclusion

A procedure for the determination of TCC, TCS and MTCS in environmental water samples is developed. The analytes were simultaneously isolated using silicon dioxide/polystyrene composite microspheres SPE sorbent, and then they were determined with UHPLC-ESI-MS. Under the optimized conditions, the LODs were 1.0 ng/L, 2.5 ng/L and 4.5 ng/L for TCC, TCS and MTCS, respectively. The spiked recoveries of TCC, TCS and MTCS in environmental water samples were achieved in the range of 89.5% - 96.8% with RSD below 5.7%. With this method, the TCC, TCS and MTCS in a variety of environmental water samples from Xiaoqing Rivers and Yellow Sea were detected. This work indicates that the proposed method is con-

Table 1.
Linear range and limits of detection of the method.

| Analyte | Linear range (ng/L) | r^2 | LOD | LOQ |
|---------|---------------------|-------|-----|------|
| TCC | 5 - 2000 | .996 | 1.0 | 3.5 |
| TCS | 5 - 2000 | .994 | 2.5 | 8.0 |
| MTCS | 5 - 2000 | .997 | 4.5 | 14.0 |

Table 2.
Experimental recoveries of TCC, TCS and MTCS from spiked real water samples.

| Analyte | Found (ng/L) | Added (ng/L) | Recovery (%) | RSD (%) |
|---------|-----------------|--------------|--------------|---------|
| TCC | 42 | 50 | 89.5 | 5.2 |
| | 136 | 200 | 93.4 | 3.8 |
| TCS | 62 | 50 | 93.8 | 4.9 |
| | 93 | 200 | 95.6 | 5.7 |
| MTCS | ND ^a | 50 | 96.8 | 3.3 |
| | ND | 200 | 94.2 | 3.9 |

Note: ^aNot detected.

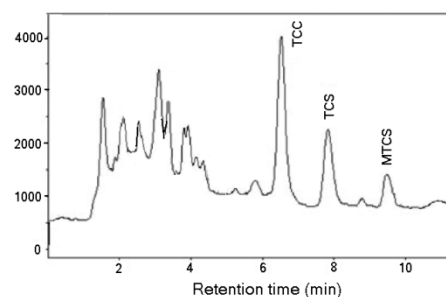


Figure 6.
Typical HPLC-ESI-MS chromatogram obtained from river water.

Table 3.
Analytical results of TCC, TCS and MTCS in environmental water samples.

| Samples | TCC (ng/L) | TCS (ng/L) | MTCS (ng/L) |
|----------------|------------|------------|-----------------|
| Xiaoqing River | | | |
| 1# | 42 | 62 | ND ^a |
| 2# | 326 | 245 | 22 |
| 3# | 136 | 93 | ND |
| Sea water | | | |
| 1# | 28 | 71 | 18 |
| 2# | ND | 12 | ND |

Note: ^aNot detected.

venient and reliable for the determination of TCC, TCS and MTCS in environmental water samples. This method could be applied to monitor TCC, TCS in various environmental water samples.

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