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Column Switching LC/MS/MS Method using Methylcellulose Immobilized Column for Quantitation of Triclosan and Triclocarban in wastewater

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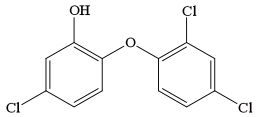
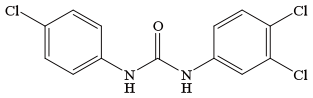
1. Introduction

Triclosan and triclocarban are antimicrobials currently added to a large number of consumer's products including household soaps, deodorants, toothpastes, mouth washes, and cleaning agents. Such release of triclosan and triclocarban has the potential to cause a number of environmental and human health problems. Triclosan is regulated all by the U.S. Food and Drug Administration, the Environmental Protection Agency, and the European Union. By wastewater treatment processes, a portion of triclosan can be degraded and partly the remaining adsorbs to sewage sludge or biosolids. In general, analysis for quantification of triclosan and triclocarban in water and solid samples has been used LC/MS/MS through the pretreatment and preconcentration. In this study, an on-line column switching pre-concentration method in which a surface modified polymer resin is used has been applied to extract triclosan, triclosan-methyl, and triclocarban in water samples. The pre-extracted chemicals were quantified using LC/MS/MS with large volume injection. The large volume injection enhances not only the LC/MS/MS throughput, but also the trapping efficiency and recovery of the analysis.

2. Experimental

2-1. Physico-chemical properties

	Triclosan	Triclocarban
Structure		
Formula	$C_{12}H_7Cl_3O_2$	$C_{13}H_9Cl_3N_2O$
Molar mass	289.54 g/mol	315.58 g/mol
pk_a	7.9	12.7
pK_{OW}	4.8	4.2

2-2. Analytical condition

1) HPLC : Shimadzu HPLC system
   - Pre-concentration : Shim-pack MAYI-ODS (G) (4.6 mmI.D. × 10 mmL., 50 µm)
   - Separation column : ACE3 C18-AR (3.0 mmI.D. × 100 mmL., 3 µm)
   - Mobile phase A / B : 5 mM ammonium formate / methanol
   - Mobile phase C : 10% Methanol in water
   - Gradient program : 70%B (5.5 min) -100%B (8-10 min) –70%B (10-20 min)
   - Flow rate A+B : 0.5 mL/min
   - Flow rate C : 1.0 mL/min
   - Injection volume : 1500 µL
   - Column temperature : 40°C

2) MS : Shimadzu LCMS-8040 Triple quadrupolemass spectrometer
   - Nebulizing gas flow : 3 L/min
   - Drying gas flow : 15 L/min
   - DL temperature : 250°C
   - BH temperature : 400°C
   - Ionization method : ESI negative ion mode
   - Data Acquisition : MRM mode (multiple reaction monitoring)
     Pause time 3 ms, Dwell time 20 ms

	Ion	Precursor ion	Product ions (CE, V)	
Triclosan	$[M-H]^-$	287	35.2 (9)	142.1 (35)
Triclocarban	$[M-H]^-$	313	160.1 (14)	126.2(20)

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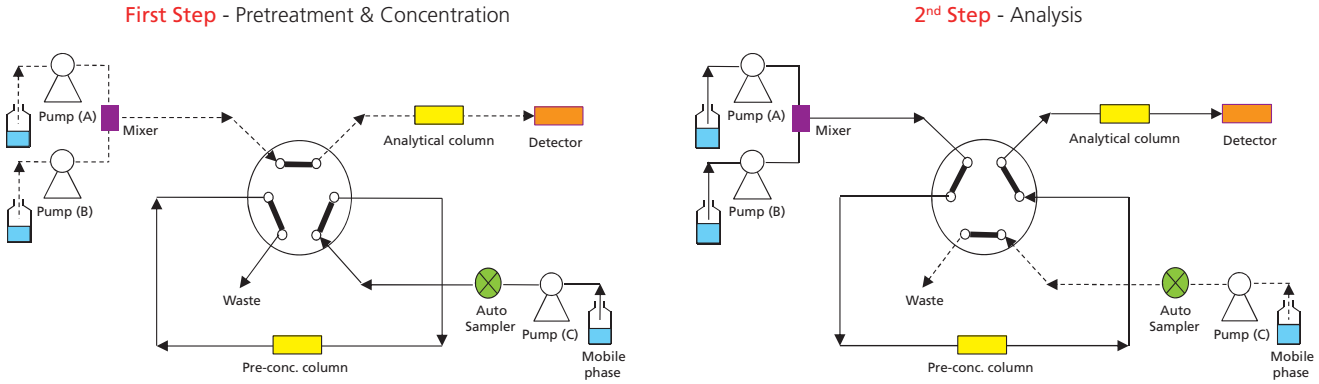
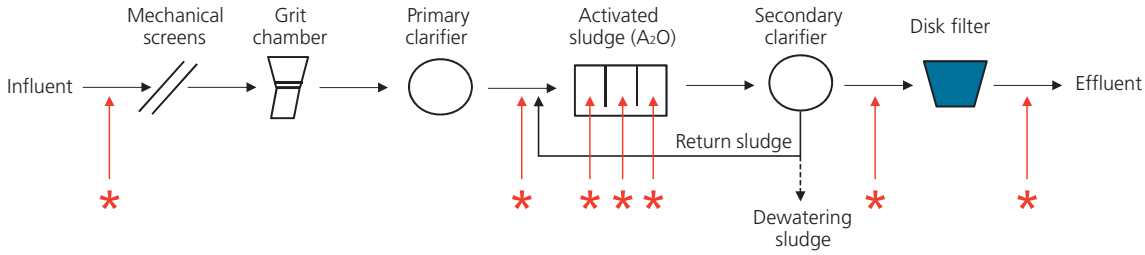


* Sample preparation – sample 1.7 mL + methanol 0.3 mL

Fig. 1 Diagram of system flow channel

2-3. Schematic diagram of sewage treatment plant under study



* Sampling points of the sewage treatment process

3. Results & Discussion

3-1. Filtration test

(n =10, ng/L)

	Triclosan			Triclocarbar		
Material	PVDF	PTFE	Cellulose Acetate	PVDF	PTFE	Cellulose Acetate
Pore size	0.2 µm	0.2 µm	0.2 µm	0.2 µm	0.2 µm	0.2 µm
Before filtration		997.1			999.6	
After filtration	591.7	887.6	493.2	616.8	925.2	514.0

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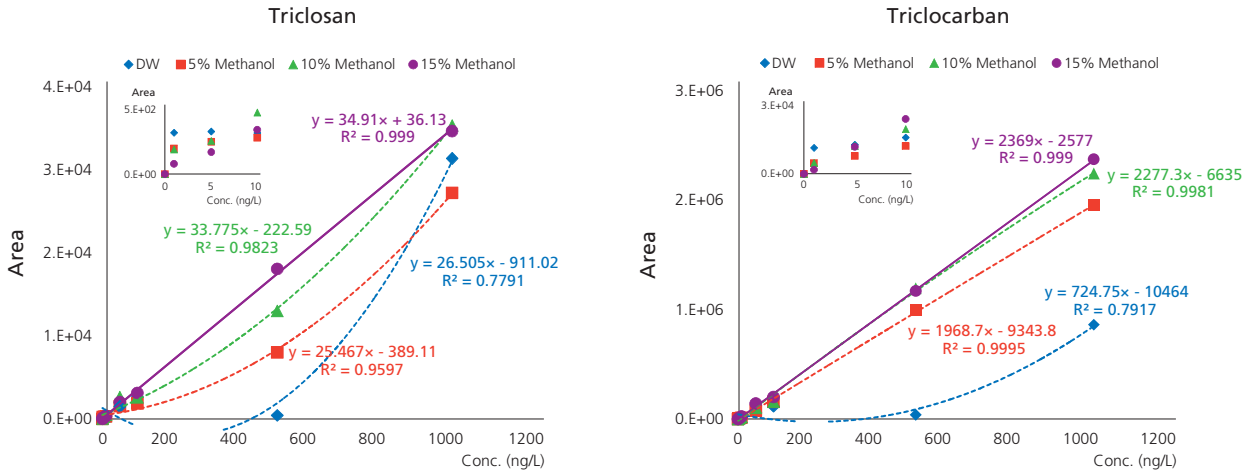
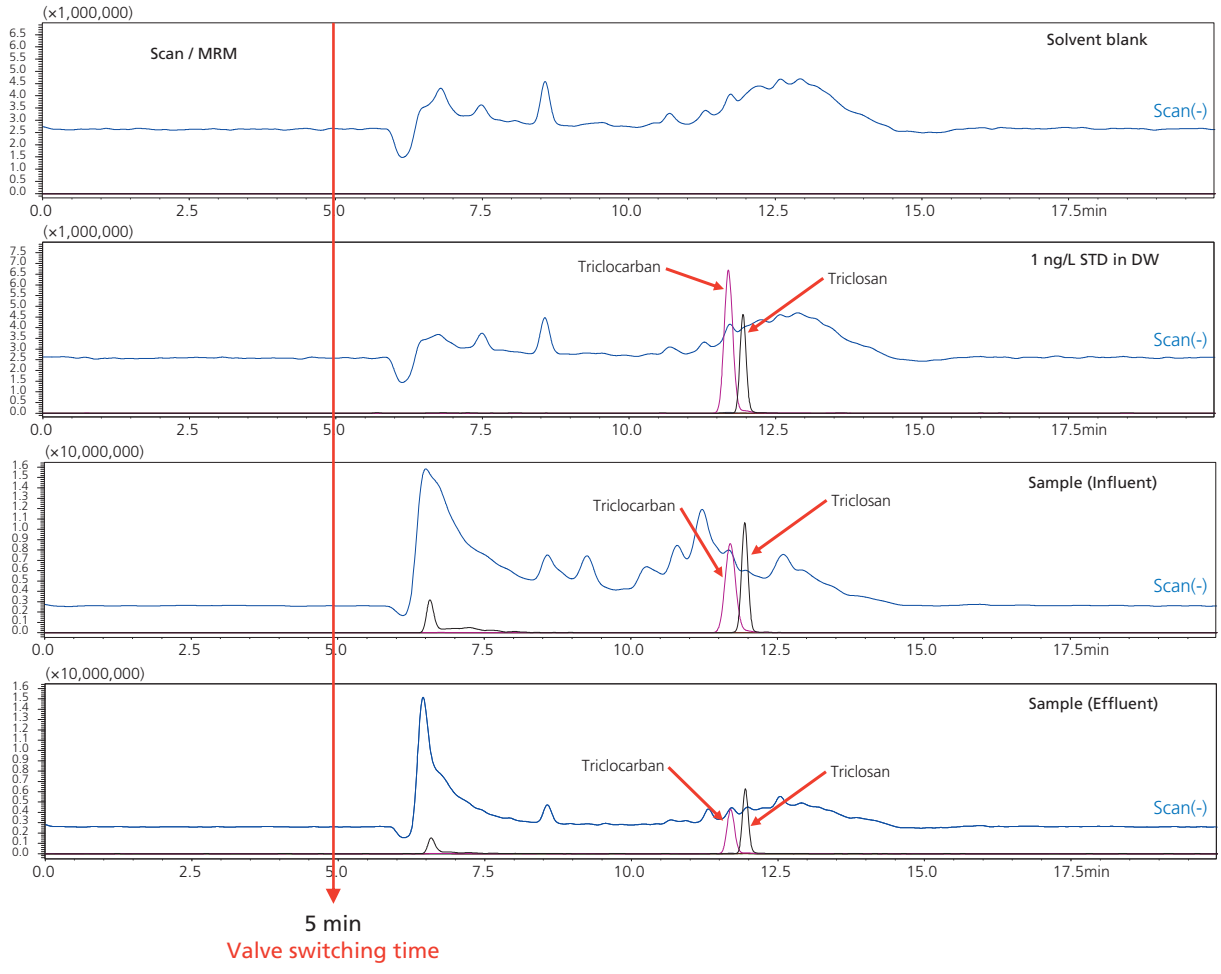
3-2. Linearities of calibration curves (n=7)



3-3. LCMS Chromatogram



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3-4. Method validation

Table 1 Recovery test

(n = 7)

		DW	Influent	Effluent	MDL(ng/L)	C.V.(%)
Trlclosan	0.1 ng/mL	98%	91%	92%	2.8	9.1
	1 ng/mL	99%	94%	91%		
Triclocarban	0.1 ng/mL	98%	91%	91%	2.5	8.1
	1 ng/mL	99%	89%	91%		

3-5. Sample analysis

Table 2 Sewage treatment plant water sample collected from each process

ng/L	Influent	Primary clarifier	Anaerobic	Anoxic	Aerobic	Secondary clarifier	Effluent
Triclosan	75	109	63	77	48	31	28
Triclocarban	72	75	48	39	47	45	38

4. Conclusion

The developed method using a methylcellulose immobilized pre-concentration column switching system could be applied successfully to quantitate residual triclosan and triclocarban without pretreatment in wastewater samples.

The preliminary finding suggests that pre-concentration method is potentially useful for on-line pre-concentration method for analysis of trace level triclosan and triclocarban in wastewater samples as well as other application.

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