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Investigation of levels and fate of triclosan in environmental waters from the analysis of gas chromatography coupled with ion trap mass spectrometry

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ABSTRACT

A gas chromatography–ion trap mass spectrometry method was developed and optimized for the analysis of triclosan in water. Tandem mass spectrometry, along with an isotope dilution internal standard method, was used for the quantitative analysis of triclosan in water at low ng l^{-1} levels. The efficiencies obtained from liquid–liquid extraction and solid-phase extraction were compared. Average recoveries by the SPE pre-concentration using a C_{18} cartridge were determined as 84–90%. The limit of detection was 2 ng l^{-1} for triclosan in water. The accuracy represented by relative analytical errors was −16% to −10%, and the precision by relative standard deviations was 3–15% ($n = 4$). The method was successfully applied to analyze triclosan at concentrations between 4.1 ng l^{-1} and 117 ng l^{-1} in environmental water samples collected from rivers and coastal water in Hong Kong.

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is a chlorinated phenoxyphenol that has been widely used as an antimicrobial or antibacterial agent in personal care products such as shampoo, soap, mouthwash, cosmetics, and cream. The chemical is also used in household cleaners and is even found in textiles and plastics, such as sportswear, shoes, carpets, and pizza-cutters due to the increasing acceptance and desire for hygienic products by the public (Okumura and Nishikawa, 1996; Schweizer, 2001; McAvoy et al., 2002; Singer et al., 2002). In Europe, about 350 tons of triclosan are presently used as an antimicrobial substance in many products (Singer et al., 2002).

Triclosan exhibits a broad spectrum of bacteriostatic activity against gram-negative and gram-positive bacteria, molds, and yeasts even at levels of 0.1–0.3% (w/w) (McAvoy et al., 2002). Moreover, some recent findings have suggested that triclosan blocks lipid biosynthesis by specifically inhibiting the enoyl-acyl carrier protein reductase (Heath et al., 1999; Levy et al., 1999; Tixier et al., 2002). The importance of fatty acid biosynthesis to cell growth and function makes the pathway an attractive target for the development as antibacterial substances. Triclosan has been extensively tested for human safety at the concentrations used in consumer products. The compound is neither acutely toxic, nor irritating to eyes and skin. Triclosan has been considered to be safe for humans when used as an antimicrobial or antibacterial agent, because of its broad safety database and history of over 30 years' usage in personal care products.

Triclosan is relatively soluble in water with a water solubility of 10 mg/l at 20 °C. The incorporation of triclosan in a vast array of products results in its discharge to wastewater treatment plants and then into surface waters. The removal of triclosan using activated-sludge treatment is approximately 96%, whereas removal with trickling-filter treatment ranges from 58% to 86% (McAvoy et al., 2002). Thus, triclosan is often detected in the aquatic environment, for example in wastewater (0.07–14000 μg l^{-1}), in seawater (50–150 ng l^{-1}), and in sediments (1–35 μg kg^{-1}) (Lopez-Avila and Hites, 1980; Okumura and Nishikawa, 1996; Lindström et al., 2002; McAvoy et al., 2002; Singer et al., 2002). Analysis of triclosan in water has been performed with LC–UV (Tixier et al., 2002), LC–MS (Hua et al., 2005) and GC–MS with selected ion monitoring technique (Okumura and Nishikawa, 1996; van Stee et al., 1999; Adolfsson-Erici et al., 2002; Lindström et al., 2002; Singer et al., 2002). Recently, ion trap mass spectrometry operated in tandem mass spectrometry (MS/MS) mode has been reported for the detection and quantitation of chlorinated environmental pollutants (Plomley et al., 2000; Cai et al., 2003; Ma et al., 2003). When operated in the MS/MS mode, the ion trap is capable of monitoring product ions of the analytes with high specificity. To the best of our knowledge, analysis of triclosan in water by using GC–ion trap MS has not been reported.

Triclosan has a pK_a of 8.1 and is photodegradable in its phenolate form. The degradation of triclosan into toxic compounds has

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become more and more of a problem, because of its extensive application and its high levels in wastewater. When textile products are treated with sodium hypochlorite (a domestic bleaching agent), or when chlorine is used in wastewater treatment plants, any triclosan present may become chlorinated at the *ortho*- and *para*-positions relative to the –OH to produce 3-chlorotriclosan, 5-chlorotriclosan and 3,5-dichlorotriclosan (Okumura and Nishikawa, 1996). Triclosan and the chlorinated triclosans have been shown to undergo both thermal and photochemical ring closure to form various toxic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs) (Okumura and Nishikawa, 1996; Latch et al., 2003; Agüera et al. 2004; Mézcua et al., 2004; Morrall et al., 2004).

Although triclosan is regarded as a compound of low toxicity, it is important to develop practical methods for its determination, because of its potential to transform into dioxins under certain conditions. The analytical method must also detect triclosan at trace levels in order to support studies on its environmental fate and behavior, which are not yet fully understood. This paper describes a gas chromatography–ion trap mass spectrometry (GC–ITMS) method developed for the investigation of levels and fate of triclosan in environmental waters in Hong Kong.

2. Experimental

2.1. Reagents and chemicals

Standards of triclosan and $^{13}C_{12}$-triclosan (isotope purity of >98%) were purchased from Wellington Laboratories (Ontario, Canada). HPLC-grade organic solvents were obtained from Labscan Analytical Science (Patumwan, Bangkok, Thailand). The silica-bonded C_{18} cartridge (500 mg) was bought from Waters Corporation (Milford, MA, USA). The stock solution was prepared by dissolving 1.0 mg of triclosan in 10 ml of ethyl acetate. The relative response factor (RRF) was determined by using the calibration standard solutions containing the analyte and the internal standard. Organic-free water was obtained using a Milli-Q water purification system (Millipore). Standard water samples were prepared by adding the analytes into 100 ml of the Milli-Q water at various concentrations.

2.2. Optimization of ion trap mass spectrometric parameters

GC–MS analysis was conducted on a Thermo Finnigan Trace gas chromatograph interfaced to a PolarisQ ion trap mass spectrometer (Austin, TX, USA). Data acquisition and processing, and instrumental control, were performed by the Xcalibur software from Finnigan. A capillary column, DB-5MS (30 m × 0.25 mm I.D., 0.25 μm film thickness, J&W), was used with the injector operating in splitless mode at a temperature of 250 °C. The injection volume was 1 μl. The helium carrier gas flow was maintained at 1 ml/min. The oven temperature program was set at 90 °C initially and held for 1 min, before being raised to 280 °C at a rate of 20 °C/min (6 min). The transfer line temperature was set at 300 °C. The mass spectrometer was operated using electron impact ionization (EI), with a solvent delay of 8 min to prevent damage to the MS filament.

The first step of the MS/MS method development was to establish the chromatographic retention time and to select an appropriate precursor ion for each analyte. A mixture of triclosan and $^{13}C_{12}$-triclosan was prepared in ethyl acetate and analyzed by GC–ITMS operating in full-scan mode. The most abundant fragment ion was selected as the precursor ion for further MS/MS analysis of each analyte. After the application of collision-induced dissociation (CID) to the precursor ion, a daughter ion was then selected with the highest abundance as the quantitation ion for each compound. The original default values of the ITMS operating parameters were set as follows: the "*q*" value was 0.45; the resonance excitation voltage (REV) was 1.0 V; the excitation time (ET) was 15 ms; the isolation time (IT) was 8 ms; the ion source temperature (IST) was 200 °C; the electron energy (EE) was 70 eV; the emission current was 250 mA; and the isolation width was 1.0 μm.

To optimize the performance of the ion trap MS/MS, five instrumental parameters were investigated in series: the "*q*" value, REV, ET, IT and IST. The effect of each parameter, as well as the operation and application of ITMS, has been thoroughly described previously (March 1997; Mandalakis et al., 2001; Cai et al., 2003; Fabrellas et al., 2004).

2.3. Water sampling

Water samples (2.5 l each) were collected on the surface from Nu Tung River, Lam Tsuen River and Victoria Harbour in Hong Kong on 19 September, 2004 and 29 January, 2005. Nu Tung River receives the effluents of the Shek Wu Hui plant, a major secondary wastewater treatment plant. Samples from this river were taken (from upstream to downstream) at Sites A, B, and C. Site B was the discharge point of the effluent; Sites A and C were located upstream and downstream from Site B with a distance of 50 m. Lam Tsuen River is supposedly for rain water collection, but there are several illegal residential wastewater entrances to the river. Sampling Site D was located at the upstream, and Site E was downstream of Site D with a distance of 50 m. Finally, the samples from Victoria Harbour were taken from four sites, and then mixed in equal amounts. Each sampling site was at least 50 m away from the next.

The samples were collected in ethanol-rinsed amber glass bottles and acidified with phosphoric acid to a pH of <2 for preservation. The collected samples were refrigerated (at 4 °C) for less than 48 h prior to the analysis. Analysis of spiked blank samples that were stored under the same conditions did not show the change of triclosan during the storage.

2.4. Water sample pre-treatment and analysis

2.4.1. Liquid–liquid extraction using dichloromethane

The liquid–liquid extraction of triclosan from water was performed using dichloromethane. The extraction recovery was determined with standard water samples fortified at 20, 200 and 2000 ng l^{-1} of triclosan. The pH of the sample was adjusted to 2, 7 and 11. The fortified water samples (at 100 ml each) were extracted three times, using 20 ml of dichloromethane every time. The extracts were combined and dehydrated with anhydrous sodium sulfate. After that, the extracts were concentrated to 1–2 ml by a rotary evaporator, and further evaporated to dryness under a slow nitrogen stream, in a water bath maintained at 40 °C. An internal standard of 20 ng $^{13}C_{12}$-triclosan was added and the extract was diluted to 100 μl by ethyl acetate. One microliter of the sample extract was injected for the GC–ITMS analysis.

2.4.2. Solid-phase extraction

The solid-phase extraction (SPE) cartridge was preconditioned with 5 ml each of ethyl acetate, methanol, and organic free water at a flow rate of 2 ml/min. The SPE extraction of triclosan was accomplished by passing 100 ml water samples, with their pH adjusted to 2, through the preconditioned cartridge at a flow rate of approximately 5–10 ml/min with air pump vacuum. After each water sample had completely passed through, the cartridge was rinsed with 5 ml of 10% methanol in water, and dried for about 10 min under vacuum. The triclosan retained in the cartridge was then eluted twice, with 2 ml of ethyl acetate each time, at a flow