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Study on detection methods for triclosan in environmental samples

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Abstract
Triclosan (TCS) has been widely used as an antibacterial and antifungal agent in household cleaning and personal care products. The widespread use of TCS in the cleaning products poses a potential risk to the ecological system and human health due to its release into sediments, wastewater and ground water resources causing chronic toxicity to aquatic organisms. Therefore, it is necessary to develop a fast, simple, and efficient method for monitoring TCS in the environment. In this article the studies of detection methods for TCS in the environmental samples in recent years are reviewed.

Keywords: Triclosan, TCS, determination, detection, sensor

1. Introduction
Triclosan (TCS) [5-chloro-2-(2,4-dichlorophenoxy) phenol], is a typical chemical in pharmaceuticals and personal care products. It has been used as an antimicrobial agent in pharmaceuticals and personal care products such as surgical suture materials or hand soaps, deodorants, detergents, shampoos, toothpastes, antiseptic-creams, plastics, food-stuffs and functional clothing for many years. In recent years there has been a significant increase in consumer products containing TCS [1-3]. Its widespread use has led to the release of TCS into wastewater, sediments and many water sources. Once in the aquatic environment, TCS can undergo a series of transformation reactions to produce, in some cases, more toxic or bio-accumulative compounds, which lead to the formation of compounds such as 2,8-dichlorodibenzo-p-dioxin, chlorinated dioxins and dichloro and trichlorophenols [4-6]. Therefore, TCS is chronically toxic to aquatic organisms and its presence in wastewaters may affect the ecosystem and human health. Nowadays, the potential risk to the environmental safe and human health generated from TCS has drawn great attention all over the world [7-9]. So a rapid and sensitive method to detect TCS in environmental samples at trace levels is very important to ensure human and environment safety. In this paper, the attributes of different analytical technique for the determination of TCS in environmental samples in recent years are reviewed.

2. Analytical Methods
2.1 HPLC method: High-performance liquid chromatography (HPLC) is a powerful tool that enables the separation of complex mixtures into individual components, and is a highly sensitive and reproducible analytical technique. In recent years, HPLC has been combined with many sensitive detection techniques and has experienced continuous improvement of stationary phases, which have improved its sensitivity and specificity. HPLC is currently widely used for the analysis of drugs and dosage forms with respect to quality control, quantitative determination of active ingredients and impurities, monitoring drug blood concentration in patients, and bioequivalence assessment [10-12].
Escarrone *et al.* [13] developed a simple, rapid and sensitive analytical method for the detection of TCS from Poecilia vivipara tissues. They developed a matrix solid phase dispersion (MSPD) extraction method followed by analysis with a LC tandem mass spectrometry system and applied the multivariate statistical approach to optimize the extraction conditions. The analytical method showed high extraction yields for the determination of this compound in a complex matrix such as tissue. Moreover, the extraction procedure was very fast and it was possible to perform on a small sample aliquot. The limit of quantification value in fish tissue was 0.083 mg g^{-1} and the limit of detection was 0.016 mg g^{-1}.

The application of the vortex-assisted MSPD method to the analysis of real samples showed TCS in some fish liver and fish gill samples at trace levels.

Sun *et al.* [14] developed a sensitive and efficient analytical method for TCS determination in water, which involved enrichment with bamboo-activated charcoal and detection with HPLC-ESI-MS. They investigated and optimized the influence of several operational parameters, including the eluant and its volume, the flow rate, the volume and acidity of the sample, and the amount of bamboo activated charcoal. Under the optimum conditions, linearity of the method was observed in the range of 0.02–20μg/L and the limit of detection was 0.002μg/L. The spiked recoveries of TCS in real water samples were achieved in the range of 97.6–112.5%. The proposed method was applied to analyze TCS in real aqueous samples.

2.2 Electrochemical method: Since the early 70s electrochemistry has been used as a powerful analytical technique for monitoring electro active species in living organisms. It is a promising alternative for the determination of organic molecules in complex matrices, because it delivers lower cost and analysis time, high selectivity, and high sensitivity. Since TCS contains the construction of phenolic hydroxyl, it is strongly suggested that this compound could undergo oxidation process at the suitable sensing interface under proper conditions [15-17].

Regiart *et al.* [18] developed a simple and sensitive electrochemical sensor with an ordered mesoporous carbon modified screen-printed carbon electrode (SPCE) to detect TCS in river water samples. Due to its high specific surface area, large pore volume, uniform mesostructure, good conductivity and excellent electrochemical activity, this porous carbon material provided selectivity and sensitivity for the electrochemical determination. The electrochemical behavior of TCS showed an irreversible oxidation peak measured by square wave voltammetry. The detection limit was 0.24 ng mL^{-1} with a wide linear range from 0.8 ng mL^{-1} to 40 ng mL^{-1}. This electrochemical platform offered a useful tool for on-site TCS determination in environmental samples.

Yola *et al.* [19] developed a novel molecular-imprinted electrochemical sensor based on gold nanoparticles decorating polyoxometalate/reduced graphene oxide for determination of trace TCS in wastewater. The sensor was found to have a linear detection range and a limit of TCS at 0.5–50.0nM and 0.15 nM, respectively. The molecular imprinted sensor was applied to wastewater and lake water samples and demonstrated effective performance as compared to other complicated methods.

2.3 Gas chromatography method: Among these different methods, gas chromatography (GC) method is a more suitable technique for analysis of TCS because of its high resolution, excellent sensitivity, inexpensive instrumentation and the availability of selective detectors, which could attain qualitative and quantitative analysis at the same time [20-22].

Azzouz *et al.* [23] proposed a highly sensitive gas chromatography–mass spectrometry (GC–MS) method for the determination of endocrine disrupting chemicals (EDCs) including parabens, alkylphenols, phenylphenol, bisphenol A and TCS in human breast milk, blood and urine samples. Analytes were retained on a LiChrolut EN column and derivatized by silylation following elution with acetonitrile. The resulting trimethylsilyl derivatives were determined by GC–MS. The proposed method exhibited good linearity for all target EDCs, and provided low limits of detection, good precision and recoveries. A total of 24 human fluid samples were analyzed and most found to contain some target EDC at concentrations from 0.10 to 14μg/l.

Shih *et al.* [24] developed a new in-tube based ultrasound-assisted emulsification microextraction technique coupled with gas chromatography-micro-electron capture detection for the efficient and rapid analysis of TCS in environmental water samples. Under optimal conditions, the method showed good linearity in the concentration range from 20–2000 ng $L^{-1}$with a correlation coefficient of 0.9982 for the target analyte. The limit of detection was 4 ng L^{-1}. The method was validated with real water samples and the relative recoveries of environmental water samples ranged between 91.2 and 97.3% and relative standard deviations ranged between 2.8 and 5.4%, making the proposed method highly reliable, which provided a simple, rapid, sensitive, low cost, easy to handle and eco-friendly procedure to determine TCS in aqueous samples.

2.4 Other methods: In addition to these main approaches mentioned above for TCS detection, still a few special techniques with high sensitivity have been applied. Atar *et al.* [25] developed a sensitive molecular imprinted surface plasmon resonance nanosensor for selective determination of trace TCS in wastewater. Cabaleiro *et al.* [26] proposed two ultrasound-assisted emulsification–microextraction procedures based on the use of a micellar ionic liquid as extractant for TCS determination in troublesome matrices such as cosmetics and wastewaters. Wang *et al.* [27] developed a novel naphthoic acid ionic liquid and applied it in "no-organic solvent microextraction" for determination of TCS and methyl TCS in human fluids. Wang *et al.* [28] developed a dispersive liquid–liquid microextraction combined with capillary zone electrophoresis–UV detection for analyzing TCS and bisphenol A in water, beverage, and urine samples.

3. Conclusions

The widespread use of TCS in household cleaning products, medical devices and personal care poses a potential risk to the ecological system and human health due to its release into sediments, surface water and ground water resources and chronic toxicity to aquatic organisms [29, 30]. Thus, the qualitative analysis of TCS is an important factor to monitor it in environmental and biological metrics. This review has highlighted the significant developments in rapid and alternative techniques for the detection of TCS in recent years. We believe the development of TCS sensors with better sensitivity and specificity, lower cost, simplicity is still the future effort.

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