Abstract

This research aims to develop a simple analytical method based on solid-phase microextraction (SPME) to simultaneously extract a variety of pharmaceutical compounds possessing differing physico-chemical properties from urban wastewater.

This study presents a sensitive and specific method for the quantitative determination of pharmaceuticals in waste waters. As a sample preparation method, SPME is an environmentally-friendly analytical technique which isolates and pre-concentrates trace organic pollutants from waste waters in a single step.

The coupling of SPME to tandem mass spectrometry capability (LC-ESI-MS/MS – TSQ Vantage) allows for identification/confirmation and quantitation in a single analysis. The quantitation limits range between 10 - 50 ng/L with relative standard deviations less than 15 % (RSD < 15 %).

Preliminary results suggest this method is capable of detecting and quantifying a range of pharmaceuticals in urban wastewater effluents collected from the Grand River near Kitchener, Ontario.

Introduction

Frequent detection and widespread distribution of emerging contaminants, such as pharmaceuticals and personal care products, are cause for increasing concern from both environmental and human health perspective.

These emerging contaminants are continually infused to aquatic ecosystem through municipal wastewater discharge, while some pharmaceuticals are removed during wastewater treatment, others are.1, 2

There is need to develop analytical method that can measure trace concentrations of these compounds in water resources.

Recently, solid phase microextraction was proposed as a simple sample preparation method suitable for extraction of pharmaceutical due to availability of sensitive tandem mass spectrometry which can be coupled with SPME.

Research Objectives

- To develop a simple analytical method based on SPME for high throughput analysis of target pharmaceuticals in waste water
- To understand the occurrence, fate and partitioning of emerging contaminant in environmental water samples

Optimization of extraction time

Experimental- SPME method (workflow)

- Selection of extraction phase
- Condition of extraction phase (fibres) in toluene solvent (5 - 15)
- Determination of extraction time
- Optimization of the method (pH and salt effect)
- Optimization of desorption solvent composition
- Analysis by LC-MS/MS

Method validation in spiked wastewater

- Limit of detection (LOD) and quantification (LOQ) of the method was determined using signal-to-noise ratios of 3 and 10, respectively in spiked wastewater (3 ng/ml).
- Precision of the method (measured as relative standard deviation, RSD < 10%) is acceptable
- Spiked concentration - 3 ng/ml

Optimization strategies

- Increased volume of the extraction phase to improve sensitivity of the method
- Increased surface area of the extraction phase for faster extraction
- Using a highly sensitive detector like mass spectrometry – TSG MS

Results and discussions

- Figure 3: Overview of SPME method
- Figure 4: Description of method development format
- Figure 5: SPME method development and validation in spiked waste water samples

Figure 6a) Comparison of extraction efficiency in PB (pH = 7.4), Pure water and waste water

Figure 6b) Effect of pH on the extraction efficiency of SPME method

Figure 6c) Effect of salt on the extraction efficiency of SPME method

Figure 6d) SPME sampling procedure and LC/MS/MS method for analysis

Figure 7a) Comparison of extraction efficiency in PB (pH = 7.4), Pure water and waste water

Figure 7b) Effect of pH on the extraction efficiency of SPME method

Figure 7c) Effect of salt on the extraction efficiency of SPME method

Figure 7d) Chromatogram of waste water of SPME extract collected from Kitchener Grand River

Figure 7e) Chromatogram of wastewater matrix on the method using fluoxetine

Figure 7f) Reproducibility of the method

Figure 7g) Concentration of analytes detected in the downstream effluent along Grand River

Summary

- Solid phase microextraction may be a promising method of analysis of pharmaceuticals in waste water
- This study demonstrates the developed method (SPME-thin film/LCMS/MS) has acceptable detection limit (low ng/L range) capable of detecting the selected pharmaceuticals in environmental water samples
- This study demonstrates the utility of SPME as a simple analytical method for microextraction of selected pharmaceuticals in waste water

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References:

Development of SPME with liquid chromatography-tandem mass spectrometry for high throughput analysis of pharmaceuticals in urban wastewater

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