

改良式固相萃取技術應用於超純水中鄰苯二甲酸酯類之微量分析

研究生：劉旭娟

指導教授：黃志彬

國立交通大學環境工程研究所

摘要

隨著積體電路的集成度和複雜性越來越高，污染控制對技術的發展影響越大，其中針對晶圓製程之超純水進行微污染控制是十分重要的。而主要有機污染物來源之一為鄰苯二甲酸酯類，此類有機物容易從聚合材質如塑膠容器及管線釋出。目前超純水中的有機物濃度通常利用儀器監測並以總有機碳表示之，但在 65 nm 製程技術下以總量表示有機物濃度之方式逐漸不適用。有鑑於此，本研究預發展一改良式固相萃取技術進行微量有機物之捕集，並評估奈米碳管作為前濃縮材料之可行性。

本研究所建立一套有效萃取濃縮超純水中之超微量鄰苯二甲酸酯類的分析方法中，首先利用蠕動幫浦在一定流速下輸送水樣使之流經過一內填疏水性吸附劑之採樣管，待水樣中之有機污染物被吸附劑吸附後再加以除去其中殘留水份，最後利用ATD/GC-MS進行分析檢測。本技術有別於現存的方法，進行萃取試驗時不會使用到任何有機溶劑，可消除來自溶劑中污染物干擾的問題因而提高靈敏度。研究顯示脫附溫度、時間、劑量、採樣流速以及除水流程為影響分析結果的主要參數。此方法所得六種鄰苯二甲酸酯類之方法偵測極限為40.3~99.98 ng/L以及回收率為12~87%。另外批次式吸附實驗之結果顯示奈米碳管對鄰苯二甲酸二乙酯的吸附容量約為活性碳的8.8倍，且其吸附行為符合 Langmuir 等溫吸附曲線。結果顯示出奈米碳管可作為前處理之濃縮材料與市售吸附劑(高分子聚合物)相比可有效萃取濃縮六種鄰苯二甲酸酯類。

附註說明：由於本研究係與工研院能資所之合作研發計畫，牽涉商業機密，對於所使用之關鍵耗材及分析條件負有保密之義務，因此本文中部份實驗條件之描述將以代號表示，以示負責。

關鍵詞：超純水、固相萃取、奈米碳管、微污染、鄰苯二甲酸酯類

Ultra-trace analysis of phthalate esters in ultrapure water by a modified solid-phase extraction method

Student : Hsu-Chuan Liu

Advisors : Chih-pin Huang

**Institute of Environment Engineering
National Chiao Tung University**

Abstract

The increasing complexity and miniaturization of modern integrated circuit demand lower defect density in the active region of the silicon devices. This, in turn, necessitates the more stringent control of ultrapure water (UPW) that represents a major source of contamination during the “wet-bench” processes. One of the most potent surface-bound organic families is the phthalate esters, which could easily release from the surface of polymeric materials such as plastic containers and pipes. The current limit of organic contaminants in UPW, normally measured by total organic carbon (TOC), becomes inadequate in addressing the organic ultra-trace contamination for the next generation of fabrication technology (< 65 nm). Therefore, the objectives of the present study are to develop a direct sampling and analytical procedure by modifying the conventional solid-phase extraction method, and to evaluate the feasibility of multi-wall carbon nanotube (MWNT) as a novel solid sorption material.

In the proposed method, UPW is delivered through a sampling tube containing hydrophobic sorbent to concentrate the aqueous phthalate esters, much similar to the air sampling procedure. The water content is then removed from the sorption tube subjected to thermal desorption and analysis by gas chromatography-mass spectrometry (GC-MS). This process removes the solvent-extraction procedure necessary for the conventional solid extraction method, thereby eliminating analytical problems associated with solvent interference. Several important parameters, including sorption/desorption temperatures and durations, packing depth, sampling flow rate, demisting procedure, are optimized in this study based on the analytical sensitivity for six different phthalate esters.

The method detection limit (MDL) and recovery rates for six different phthalate esters are approximately 40.3~99.98 ng/L and 12~87%. The adsorption capacity of DEP onto MWNTs (8.55 mg/g) is approximately 8.8 times higher than onto GAC (0.965 mg/g), and followed a Langmuir-type adsorption isotherm. The results showed that the MWNTs exhibited greater adsorptivity for the six tested phthalate esters as compared to the polymeric sorbents.

Keywords: Ultrapure water, Solid extraction, Carbon nanotube, Trace contamination, Phthalate esters