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# Comparison of electrospray ionization, atmospheric pressure chemical ionization and atmospheric pressure photoionization for determining estrogenic chemicals in water by liquid chromatography tandem mass spectrometry with chemical derivatizations

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## ABSTRACT

This study compared the sensitivities and matrix effects of four ionization modes and four reversed-phase liquid chromatographic (LC) systems on analyzing estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3), 17 $\alpha$ -ethinylestradiol (EE2), 4-nonylphenol (NP), 4-*tert*-octylphenol (OP), bisphenol A (BPA) and their derivatives of dansyl chloride or pentafluorobenzyl bromide (PFBB) in water matrices using a triple-quadrupole mass spectrometer with selected reaction monitoring (SRM). The four probes were electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI) and APCI/APPI; the four LC systems were ultra-performance liquid chromatography (UPLC) with or without post-column split, a mixed-mode column and two-dimensional LC (2D-LC). Dansylated compounds with ESI at UPLC condition had the most intense signals and less matrix effects of the various combinations of ionization and LC systems. The on-column limits of detection (LODs) of dansylated estrogens by SRM were 0.05–0.20 pg, and the LODs in sewage treatment plant effluent and in river water were 0.23–0.52 and 0.56–0.91 ng/L, respectively. The LODs using selected ion monitoring (SIM) reached low ng/L levels in real samples and measured concentrations were comparable with those of SRM.

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## 1. Introduction

Feminizing contaminants of steroid estrogens, detergent degradates and plasticizers have caused a worldwide concern. They may influence the ecosystem at trace levels and affect human health through their contamination of drinking water. Natural estrogens 17 $\beta$ -estradiol (E2) and its synthetic analogue 17 $\alpha$ -ethinylestradiol (EE2), an ingredient in oral contraceptives, are the most estrogenic. Moreover, their major metabolites, estrone (E1) and estriol (E3), are still bioactive. These steroid estrogens enter the water environment via the urine of humans and animals in the form of hydrophilic glucuronide and sulfate conjugates [1], which are biologically inactivated [2]. However, they are likely to be deconjugated in sewage treatment systems and converted to estrogenically active free forms [3]. 4-nonylphenol (NP), 4-*tert*-octylphenol (OP) and bisphenol A (BPA), which are all xenoestrogens, can affect normal endocrine functions. Although they are less potent, they are usually found in much higher concentrations in water (ng/L– $\mu$ g/L) [3–6]. These

xenoestrogens are released into the water environment from daily usage of non-ionic surfactants and plasticizers.

Atmospheric pressure photoionization (APPI) is an emerging source, which is capable of ionizing nonpolar compounds and is possibly less susceptible to matrix effects. In addition, dual-source ionization (e.g. atmospheric pressure chemical ionization (APCI)/APPI combo in this study) expands the range of compounds that can be simultaneously analyzed. Although most studies determined feminizing chemicals with electrospray ionization (ESI) coupled with LC/MS(/MS) [7–9], the suitability of APCI and APPI deserve further exploration.

Matrix effect, which co-eluting components from the matrix or the mobile phase may enhance or suppress signals, is an important issue in using LC/MS/MS. Selective extraction, additional clean-up, efficient LC separation or change of mobile phase compositions may reduce matrix effects [10]. Furthermore, while the use of suitable internal standards (e.g. isotope-labeled chemicals) may correct signal irreproducibility, this approach will not be able to overcome the loss in sensitivity caused by matrix effects. Some studies utilized direct online extraction or post-column split to minimize matrix effects and simplify the sample preparation. A novel column developed on September 2006 combines both size exclusion and

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