# Abstract

Environmental endocrine disruptors, including natural and synthetic steroid estrogens such as 17β-estradiol (E2), estrone (E1), estriol (E3), and 17α-ethinyl estradiol (EE2), have caused concerns for the disruption of the aquatic ecosystem and human health effects. Although the concentrations of steroid estrogens (pg/L~ng/L) are lower than those of other compounds known as feminizing agents, their effects may be more significant because of their high potencies. Due to their chemical properties and trace levels in the environment, LC/API/MS may not achieve sufficient sensitivity, especially for complex water matrixes. To enhance the signals of the analytes, structure modifications of estrogens with appropriate derivatization reagents are promising to improve detection limits by increasing the ionization efficiency on MS.

In this study, three selected derivatization reagents of different modification mechanisms were used to enhance the detection of steroid estrogens in waters, and the objective was to evaluate the impact of environmental matrixes on their performance. Based on the structural feature of steroid estrogens, which contain a phenolic group, dansyl chloride, 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS), and pentafluorobenzyl bromide (PFBBr) were selected as the derivatization reagents.

The derivatized products of dansyl chloride provided higher signal intensity up to one or two orders than that of underivatized estrogens under the conditions without matrix effects. The derivative signals of FMPTS

seemed to be analyte-dependent; derivatized products of E1, E2, and EE2 gained signal enhancement ranged from 2.19 to 12.1 times, whereas derivatized products of E3 showed poor signal intensity that was even worse than underivatized E3. Signal intensities of the four target compounds were enhanced consistently up to 5.81 times with PFBBr derivatization. When the derivatization methods were applied to real water samples, including river water, drinking water and effluents from the sewage treatment plant (STP), severe matrix effects were observed in the procedures using electrospray ionization (ESI), but were insignificant in atmospheric pressure chemical ionization (APCI) operation. Considering both sensitivity enhancement and matrix effect, this study suggested utilizing the dansyl chloride derivatization method in samples with less matrix effect such as drinking water, and the PFBBr derivatization method for complex environmental matrixes such as river water and STP effluents.

This study presented qualitative comparisons of these derivatization methods. Further method validation and quantitative analysis is desired to analyze steroid estrogens in environmental waters.

*Key words*：Chemical derivatization； LC/MS/MS； Matrix effect