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Determination of fluorescent whitening agents in laundry detergents and surface waters by solid-phase extraction and ion-pair high-performance liquid chromatography

Wei-Chuan Shu, Wang-Hsien Ding*

Department of Chemistry, National Central University, Chung-Li 32054, Taiwan

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Abstract

A simple method was developed to detect four stilbene-type disulfonate and one distyrylbiphenyl-type fluorescent whitening agents (FWAs) in household laundry detergents and surface waters by ion-pair high-performance liquid chromatography. The FWA concentrations in detergents were measured directly. The contents of FWAs in water samples were extracted by solid-phase extraction (C_{18}-SPE) with ion-pairing reagent, and were then determined by an isocratic ion-pair chromatography (IPC) using a C_{18} column, applying tetrabutylammonium hydrogensulfate (TBA) as the ion-pairing reagent in mobile phase, and equipped with fluorescence detection. Water samples at various pH conditions for SPE were evaluated. Experimental results indicate that the proposed method is precise and sensitive in analyzing FWAs, and enables quantitation of 0.01–0.1 μg/l in 100 ml water samples. The recovery rates of FWAs in spiked water samples were between 73 and 89%, and the precision (RSD) ranged from 2.6 to 8.9%. Over 7200 μg/g of 4,4′-bis(2-sulfostryl)-biphenyl (DSBP) and 2320 μg/g of 4,4′-bis[(4-anilino-6-morpholino-1,3,5-triazine-2-yl)-amino]stilbene-2,2′-disulfonate (DAS1) were detected in household laundry detergents. Trace amounts of DSBP were detected in surface water samples ranging from 0.2 to 3.7 μg/l.

Keywords: Fluorescent whitening agents; Laundry detergents; Surface waters; High-performance liquid chromatography; Solid-phase extraction

1. Introduction

Fluorescent whitening agents (FWAs) are frequently added to household laundry detergents to enhance the “whiteness” and “brightness” characteristics of laundered fabrics. The most used FWAs in laundry detergents are diaminostilbenes and distyrylbiphenyl [1,2]. After use, the FWAs that remain in the washing liquor are usually discharged through wastewater treatment facilities or directly discharged to surface waters. Although the concentrations measured in the environmental samples were far below those expected to represent an ecotoxicological risk, and exhibited no biodegradability [3–6], most investigations in this area have focused on the transformation of FWAs in sewage treatment, and the fate and concentrations of FWA residues in the aquatic environment infected by sewage treatment plants (STP) effluents [5,7–14]. No information is available on the occurrence and concentration of FWA residues in household wastewater discharged directly into the aquatic environment. This is an important area for study because household wastewater directly discharged into the aquatic environment is a significant source of surface water contamination in many developing countries due to deficient wastewater treatment. Additionally, information on the content of FWAs in most household laundry detergents in Taiwan is unavailable. None is labeled as containing FWAs. Accordingly, the concentration of FWAs in laundry detergents and their associated environmental occurrences are not assessable, and concentrations of FWAs in surface water could not be evaluated. The widespread use of FWAs, and the increasing public concern over environmental issues have stimulated our interest to investigate the content and distribution of FWAs in household laundry detergents and surface water samples. Fig. 1 shows structures of four stilbene-type disulfonate salts and one distyrylbiphenyl-type

* Corresponding author. Tel.: +886 3 4227151x5905; fax: +886 3 4227664.
E-mail address: wding@cc.ncu.edu.tw (W.-H. Ding).

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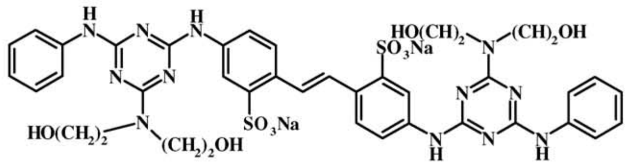
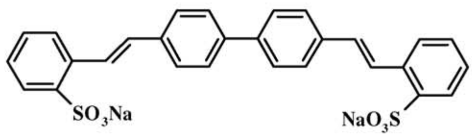
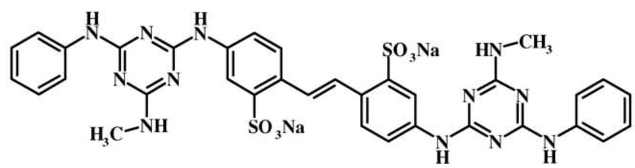
(1) 4,4'-bis{[(4-anilino)-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl]amino}stilbene-2,2'-di sulfonate (**C.I.28**) disodium salt



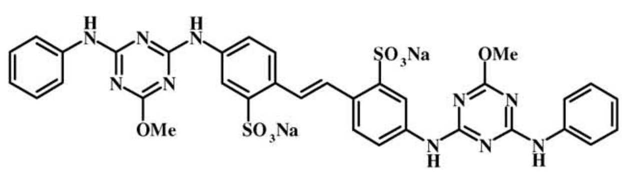
(2) 4,4'-bis(2-sulfostyryl)biphenyl (**DSBP**) disodium salt



(3) 4,4'-bis[4-(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate (**C.I.205**) disodium salt



(4) 4,4'-bis[4-(4-anilino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate (**C.I.134**) disodium salt



(5) 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene- 2,2'- disulfonate (**DAS1**) disodium salt

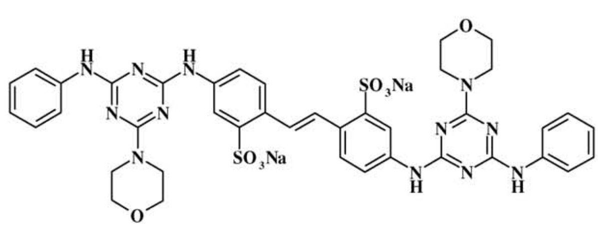


Fig. 1. Structures of FWAs used for method evaluation in this study.

FWA standards used in method development and evaluation in this study.

Determination of FWAs was performed by thin-layer chromatography (TLC) and direct spectrophotometric method [5,15–17]. In these methods, the individual FWAs were not separated, and only total FWA concentrations can be measured. It is not a problem for the routine characteristic monitoring, however, quantitation of individual FWA concentration is critical in investigating the risk assessment of FWAs due to their different toxic effects. Since 1976, high-performance liquid chromatography (HPLC) has been used to separate and determine FWAs in detergents and environmental samples [7–14,18–21]. Moreover, combining HPLC and MS with electrospray has also been reported as a powerful method for determining FWAs in detergents [22,23], and then used to identify the structures of unknown brighteners in detergents.

In this study, we developed a simple and sensitive method to routinely determine these FWAs in laundry detergents and surface water samples by applying an isocratic ion-pair chro-