

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

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Available online 3 February 2005

## 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  $\mu\text{g}/\text{l}$  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  $\mu\text{g}/\text{g}$  of 4,4'-bis(2-sulfostryl)-biphenyl (DSBP) and 2320  $\mu\text{g}/\text{g}$  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  $\mu\text{g}/\text{l}$ .

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**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 en-

vironment 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

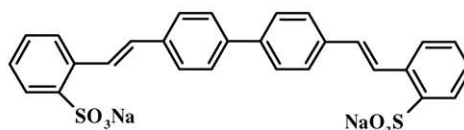
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- (1) 4,4'-bis[[4-(4-anilino)-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl]amino]stilbene-2,2'-disulfonate (C.I.28) disodium salt



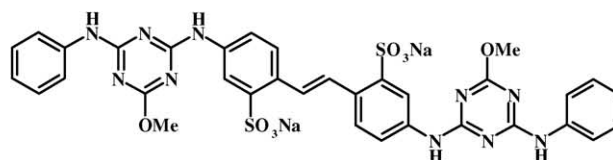
- (2) 4,4'-bis(2-sulfostyryl)biphenyl (DSBP) disodium salt



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

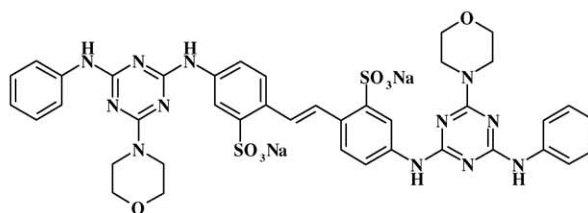


Fig. 1. Structures of FWAs used for method evaluation in this study.

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-

matographic method (IPC) with C<sub>18</sub> reversed-phase column and equipped with fluorescence detection. The precision and recovery efficiency of the SPE methods in various pH conditions were evaluated, and the effectiveness of the method in determining the contents of FWAs in household laundry detergents and surface water samples has been demonstrated.

## 2. Experimental

### 2.1. Chemicals and reagents

Unless noted otherwise all high purity chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA), Tedia (Fairfield, OH, USA) and Merck (Darmstadt, Germany), and were used without further purification. Reagent grade tetrabutylammonium hydrogen-sulfate (TBA) was purchased from TCI (Tokyo Chemical Industry, Inc., Tokyo, Japan). Reagent grade four stilbene-type disulfonate and one distyrylbiphenyl-type FWAs: C.I.28, DSBP, C.I.205, C.I.134, DAS1 were kindly supplied by Professor S.P. Wang of Providence University, Taiwan. Stock solutions of each analyte (1000 µg/ml) were prepared in methanol. Mixtures of the analytes for working standard preparation and sample fortification were also prepared in methanol. All stock solutions and mixtures were stored at  $-10^{\circ}\text{C}$  in the dark.

### 2.2. Sample preparation

The household laundry detergents as liquid or powder forms were purchased from local supermarkets or nationwide wholesale markets. The liquid detergents were diluted with methanol directly. The appropriate amounts of powder detergents were dissolved in deionized water and then diluted with methanol. The surface water samples were analyzed according to methods developed by Hayashi et al. [14], and was used with modifications. Firstly, the samples were filtered through glass fiber filter (F/G grade, Gelman Scientific, Ann Arbor, MI, USA). FWAs in filtrates (100 ml) were mixed with an ion-pairing reagent, tetrabutylammonium hydrogensulfate (TBA, 0.01 M) and adjusted to pH 8.0 (between pH 5, 7 and 8, pH 8 being optimal, see Section 3.2), and extracted by RP-C<sub>18</sub> (Supelclean ENVI-18 SPE, 3 ml, 0.5 g, surface area 500 m<sup>2</sup>/g, from Supelco, Bellefonte, PA, USA) or PS-DVB (polystyrene-divinylbenzene, LiChrolut<sup>®</sup> EN) polymeric sorbent (3 ml, 0.2 g, surface area 1200 m<sup>2</sup>/g, from Merck) cartridges, and then eluted with 5 ml methanol. The eluates were then evaporated to 100 µl, and made ready for HPLC analysis. To prevent HPLC column blockage, all samples or extracts were filtered through a glass-fiber filter prior injection.

### 2.3. HPLC analysis

The procedure used for ion-pair HPLC analysis has been reported previously [24], and was used with isocratic elu-

tion rather than gradient elution. Analyses were performed on a HP-1100 high-performance liquid chromatograph system coupled with a fluorescence detector (Agilent, Palo Alto, CA, USA). The fluorescence detection was operated at an excitation wavelength of 350 nm and an emission wavelength of 430 nm. A Hypersil ODS C<sub>18</sub> column (25 cm × 0.46 cm I.D., 5 µm packing, Agilent, Palo Alto, CA, USA) was used at a flow rate of 1.0 ml/min at ambient temperature ( $20 \pm 2^{\circ}\text{C}$ ), and the injection volume was 20 µl. Isocratic elution was performed by a 50% of acetonitrile solution with 0.4% (w/v) of TBA for 12 min.

## 3. Results and discussion

### 3.1. Optimization of HPLC separation

These FWAs are very acidic ( $\text{p}K_{\text{a}} < -1$ ) and strong hydrophilic, all separations were performed under conditions in which only the negatively charged form of the analytes were present, the analytes therefore could not be separated by a simple HPLC method. According to our previous report that involved ion-pair chromatography (IPC), separation was most effectively achieved by isocratic elution with 0.4% (w/v) TBA in 50% acetonitrile solution at pH 8.0 [25]. Gradient elution is not recommended for performing IPC separation because the separation mechanism of IPC is more complicated than that of regular reversed-phase HPLC [26]. Separation improved markedly when TBA was used as an ion-pairing reagent, perhaps because the long alkyl groups of tetraalkylammonium salts increased the interaction between the analyte and the C<sub>18</sub> stationary phase, and improved the selectivity in the reversed-phase HPLC column [25]. When the TBA concentration reached to 0.4% (w/v), a similar improvement in the baseline separation was observed for DSBP and C.I.205 [25]. The elution order is C.I.28, DSBP, C.I.205, C.I.134 and DAS1.

### 3.2. Optimization of SPE

The efficiency of SPE depends on the type of sorbent, the sample volume and its pH, the content of organic modifier and the volume of the elution solvent. Moreover, the enrichment of multiply charged compounds on hydrophobic extraction materials always requires the addition of salts or ion-pairing reagents to the water samples to increase the solute-sorbent interaction [27,28]. This fact was confirmed in our C<sub>18</sub>-SPE experiments, in which relatively high recoveries were obtained for the spiked water samples that contained 0.01 M TBA. A breakthrough for extraction of 100 ml of a spiked water sample (with 0.01 M TBA) was examined using tandem cartridges, and no significant amounts of analytes (<3%) were detected in eluate from the second cartridge. The interaction between the ion-paired FWAs and C<sub>18</sub>-SPE cartridge seems to be sufficiently strong to support quantitative extraction. Various pH values of water samples were evaluated to

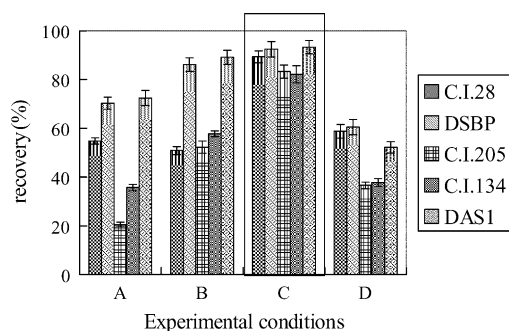


Fig. 2. Extraction recoveries of FWAs from a spiked water sample in various conditions, the extraction conditions were described in text. Extractions were performed on three replicates, standard deviation is reported as an error bar.

assess the optimal conditions. Fig. 2 reveals that adjusting pH of the spiked water samples from 5, 7 to 8 (from experimental condition A, B to C, respectively) with 0.01 M TBA, maximized recoveries (83–94%) and the reproducibility (with an RSD of around 3%). Methanol (5 ml) was found to be an appropriate elution solvent, and no ion-pairing reagent (i.e., TBA) was required in the elution solvent; this situation therefore differed somewhat from that reported elsewhere [7]. Furthermore, the highly hydrophobic PS-DVB sorbent was also investigated, when 0.01 M TBA was added to a spiked water sample at pH 8.0, lower recoveries of all FWAs (40–64%) were observed (condition D). These results indicate that the best conditions for extracting of FWAs from water samples using C<sub>18</sub>-SPE cartridges were achieved by adjusting the pH of the water sample to 8.0, and adding 0.01 M TBA as an ion-pairing reagent. To determine the efficiency and precision of the method, three replicate analyses were performed using a spiked dormitory effluent and three river water samples (Table 1). The recoveries exceeded 73%, and the precision

represented by the relative standard deviation (RSD) ranged from 2.4 to 8.9%. The results show that the method is suitable for the determining of FWAs in surface water samples.

### 3.3. Method validation

The analytical characteristics of the method, such as linear response range, reproducibility and quantitation limit, were investigated to evaluate the efficiency of the method and the possibility of the method application to real water samples. The linearity of FWAs was calculated from the five-level calibration curve over the range from 0.05 to 500 ng/ml for DSBP, and 0.5–5000 ng/ml for other four FWAs. The precisions of the curves as indicated by RSD of calibration factors (CF = peak area/amount) were 4.5–8.7%. The correlation coefficients ( $r^2$ ) exceeded 0.999. The curves covered the range equivalent to the concentrations of FWAs in the detergent samples following appropriate dilution. These five FWAs yield excellent responses and wide linearity to fluorescence detection [29], and the quantitation limits were 0.01–0.1  $\mu\text{g/l}$  (Table 1), with signal-to-noise ratios  $\geq 10$ . These results reveal that the isocratic ion-pair HPLC with fluorescence detection for the analysis of these five FWAs, ensures high reproducibility with excellent linearity and sensitivity.

### 3.4. Application to detergents and surface water samples

The versatility of this method is demonstrated in Table 1, which lists the recovery of the spiked samples (final concentrations of 0.1  $\mu\text{g/l}$  for DSBP and 1.0  $\mu\text{g/l}$  for other four FWAs) and the concentrations of FWAs detected in the water samples. The recoveries from SPE were above 73%, and the RSD ranged from 2.4 to 8.9% (as described in Section 3.2).

Table 1  
Concentration ( $\mu\text{g/l}$ ) of FWAs in surface water samples and their spiked recoveries

Water samples	FWAs ( $\mu\text{g/l}$ )				
	C.I.28	DSBP	C.I.205	C.I.134	DAS1
NCU-dormitory effluent					
Background concentration ( $\mu\text{g/l}$ )	n.d.	1.7 <sup>a</sup> (3.4) <sup>b</sup>	0.2 (3.7)	0.3 (3.5)	0.2 (3.0)
Spiked recovery (%)	87 <sup>c</sup> (3.8) <sup>b</sup>	88 (4.1)	85 (3.3)	81 (2.4)	83 (3.7)
Nan-Kan river site-I					
Background concentration ( $\mu\text{g/l}$ )	n.d.	0.2 (5.8)	n.d.	n.d.	n.d.
Spiked recovery (%)	89 (5.7)	89 (7.3)	82 (8.2)	75 (7.6)	74 (8.9)
Nan-Kan river site-II					
Background concentration ( $\mu\text{g/l}$ )	n.d.	n.d.	n.d.	n.d.	n.d.
Spiked recovery (%)	87 (3.5)	89 (5.2)	83 (4.3)	78 (3.9)	73 (4.7)
Lao-Jie river					
Background concentration ( $\mu\text{g/l}$ )	n.d.	3.7 (4.6)	n.d.	n.d.	n.d.
Spiked recovery (%)	89 (3.2)	89 (2.9)	88 (2.6)	87 (5.0)	88 (4.4)
IDL ( $\mu\text{g}$ )	2.0	0.2	2.0	2.0	2.0
LOQ ( $\mu\text{g/l}$ )	0.1	0.01	0.1	0.1	0.1

IDL: instrumental detection limits; n.d. not detected at limits of quantitation (LOQ).

<sup>a</sup> Concentration ( $\mu\text{g/l}$ ) of FWAs found in water sample.

<sup>b</sup> The relative standard deviations (RSD%) are given in parentheses,  $n = 3$ .

<sup>c</sup> The spiked recovery (%) at a final concentration of 0.1  $\mu\text{g/l}$  for DSBP and 1.0  $\mu\text{g/l}$  for other four FWAs.

Table 2  
Contents of FWAs found in household laundry detergents

Laundry detergent	FWAs ( $\mu\text{g/g}$ )				
	C.I.28	DSBP	C.I.205	C.I.134	DAS1
<b>Liquid forms</b>					
Detergent-1	n.d.	0.5 <sup>a</sup> (0.8) <sup>b</sup>	n.d.	n.d.	n.d.
Detergent-2	n.d.	165 (1.4)	n.d.	n.d.	n.d.
Detergent-3	n.d.	n.d.	n.d.	n.d.	n.d.
Detergent-4	n.d.	1490 (2.2)	n.d.	n.d.	n.d.
Detergent-5	n.d.	7200 (1.9)	n.d.	n.d.	n.d.
Detergent-6	n.d.	0.6 (0.3)	n.d.	n.d.	n.d.
Detergent-7	n.d.	n.d.	n.d.	n.d.	n.d.
Detergent-8	n.d.	3.2 (0.7)	n.d.	n.d.	n.d.
Detergent-9	n.d.	165 (1.0)	n.d.	n.d.	n.d.
Detergent-10	n.d.	1.5 (0.8)	n.d.	n.d.	n.d.
<b>Powder forms</b>					
Detergent-11	n.d.	1.5 (0.5)	7.4 (0.9)	69 (1.5)	2320 (1.2)
Detergent-12	n.d.	366 (0.4)	n.d.	n.d.	29 (0.6)
Detergent-13	n.d.	300 (1.1)	n.d.	12 (1.3)	510 (2.1)
Detergent-14	n.d.	n.d.	n.d.	23 (1.2)	610 (0.5)
Detergent-15	n.d.	n.d.	n.d.	n.d.	n.d.
Detergent-16	n.d.	0.7 (1.3)	n.d.	n.d.	n.d.
<b>Collar wash liquid</b>					
Detergent-17	0.4 (1.0)	n.d.	n.d.	n.d.	n.d.
Detergent-18	1.8 (0.6)	n.d.	n.d.	n.d.	n.d.
Detergent-19	2.1 (1.2)	n.d.	n.d.	n.d.	n.d.
LOQ ( $\mu\text{g/g}$ )	0.1	0.01	0.1	0.1	0.1

n.d.: Not detected at limits of quantitation (LOQ).

<sup>a</sup> Concentration ( $\mu\text{g/g}$ ) of FWAs found in sample.

<sup>b</sup> The relative standard deviations (RSD%) are given in parentheses,  $n = 3$ .

Table 2 lists the contents of FWAs detected in household laundry detergents, 19 laundry detergents were used as test samples after they were appropriately diluted. Fig. 3 shows the typical isocratic ion-pair HPLC chromatograms obtained from (a) a standard mixture, (b) liquid-detergent-8 and (c) powder-detergent-14. Fluorescence detection of these FWAs is highly sensitive and selective due to the high fluorescence quantum yields and the relatively high wavelength of the maximum fluorescence, which sets these FWAs apart from the most naturally-occurring interferences. Combined with the baseline separation of each analyte, the target peaks were identified by comparison with the retention times of the standard solutions and could be verified by the standard addition of target compounds, and quantities were calculated using calibration factors (CF). The results show that almost all liquid detergents, from various manufacturers, exhibited a considerable range of DSBP from 0.5 to 7200  $\mu\text{g/g}$ ; DSBP and DAS1 were found in powder detergents at levels from 0.7 to 2320  $\mu\text{g/g}$ ; a relatively low concentration of C.I.28 was detected in the collar-washing liquid. The ranges of concentrations are consistent with those determined in other reports [21,23]. However, no manufacturer labeled its product as containing FWAs.

With respect to the surface water samples, low  $\mu\text{g/l}$  concentrations of DSBP were detected in the effluent from the dormitory on the university campus and in the river wa-

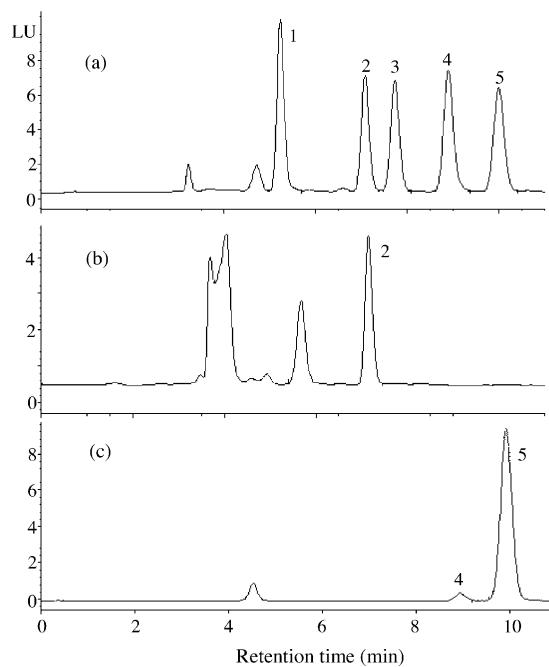


Fig. 3. Typical isocratic ion-pair HPLC chromatograms obtained from (a) a standard mixture, (b) liquid-detergent-8 and (c) powder-detergent-14. Peaks: (1) C.I.28, (2) DSBP, (3) C.I.205, (4) C.I.134 and (5) DAS1.

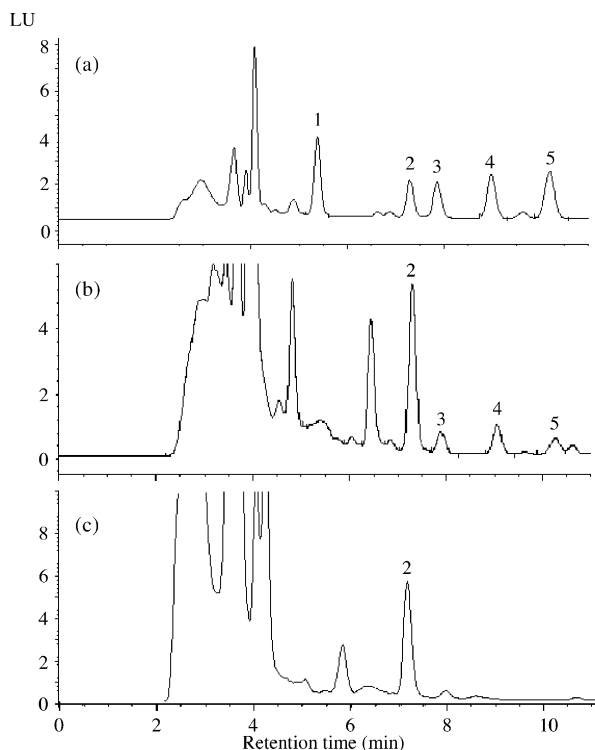


Fig. 4. Typical chromatograms of the ion-pair HPLC obtained for (a) FWAs standard mixture recovered from SPE; and for water samples from (b) NCU-dormitory effluent and (c) Lao-Jie River. Peaks: (1) C.I.28, (2) DSBP, (3) C.I.205, (4) C.I.134 and (5) DAS1.

ter samples taken near the cities. Trace amount of C.I.205, C.I.134 and DAS1 were detected in the dormitory effluent (Table 1). The results are similar to those reported in Switzerland (2.6–8.9  $\mu\text{g/l}$  in secondary effluent; 0.04–0.57  $\mu\text{g/l}$  in river water) [7] and Japan (0.68–12.5  $\mu\text{g/l}$  in secondary effluent; 0.1–6.4  $\mu\text{g/l}$  in river water) [14]. Fig. 4 displays typical chromatograms of the ion-pair HPLC obtained for (a) an FWAs standard mixture recovered from SPE; and for water samples from (b) NCU-dormitory effluent and (c) Lao-Jie River. This ubiquitous distribution is consistent with the extensive use of laundry detergents that contain FWAs and the direct discharge of household wastewater into the rivers as described above.

#### 4. Conclusions

The analytical procedure developed herein demonstrates that a  $\text{C}_{18}$  solid-phase extraction and ion-pair HPLC method is a reliable process, which is sensitive and represents a convenient analytical technique for determining FWA in household laundry detergents and surface water samples. The chosen pH, the concentration of the ion-pairing reagent in the sample, and the sorbent of SPE, are the three parameters that most influence the efficiency of the extraction of these five FWAs by SPE. The preliminary results in this study revealed that FWAs are used extensively in household laundry

detergents in Taiwan. The survey is currently being undertaken across Taiwan to determine the content of FWAs in household products. Although the toxicological information available on FWAs is limited, this study may provide further insights to promote environmental protection and conservation, and to support pollution control policies and sustainable development in Taiwan.

#### Acknowledgement

This research was supported by a grant from the National Science Council of Taiwan under contract No. NSC 93-2113-M-008-014.

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