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Determination of Fluorescent Whitening Agents in Cosmetics and Liquid Detergent by High-Performance Liquid Chromatography with Diode Array Detector in Tandem with Fluorescence Detector

YU-XIANG GU, JIN-QIN YANG, SI-YI PAN, LEI WANG, and ZE-LIN ZHOU, *Shanghai Institute of Quality Inspection and Technical Research, Shanghai 200233, People's Republic of China (Y.-X.G., J.-Q.Y., S.-Y.P., L.W., Z.-L.Z.)*

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Synopsis

Five distyryl-type fluorescent whitening agents (FWA85, 210, 220, 351, and 353) were determined in cosmetics and liquid detergent by high-performance liquid chromatography with diode array detector in tandem with fluorescence detector. The samples were extracted with ultrasound in 33% acetonitrile for 10 minutes and the components were determined by ion-pair chromatography on an MG C18 column. The limits of detection were from 0.01 to 0.1 $mg \cdot kg^{-1}$ and the limits of quantification were from 0.04 to 0.4 $mg \cdot kg^{-1}$. The recovery was from 80.7 to 103.3%. A linear relationship was present from 0.10 to 100 $\mu g \cdot ml^{-1}$ of FWAs. The protocol was simple, sensitive, selective, and was successfully applied to analyze distyryl-type FWAs in cosmetics and liquid detergent. FWA351 and FWA85 were detected in several samples with the concentrations of 19.4–1,130 $mg \cdot kg^{-1}$.

INTRODUCTION

Fluorescent whitening agents (FWAs) belong to the colorless or weakly colored organic compounds in solutions or on substrates, which could enhance the optical impression of whiteness and brightness through absorbing light in the UV range (290–400 nm) and emitting visible blue light (400–480 nm). They are numerous in variety with different structural properties. The main types of FWAs include distyryl-type, benzoxazole-type, pyrazoline-type, and coumarin-type; the distyryl-type is the most widely used product. Now FWAs extensively apply in textiles, paper manufacturing, household detergents, plastic products, and cosmetics to eliminate the yellowish cast of white fabrics and increase the whiteness and brightness of products (1–4).

Usage of FWAs in detergent could be traced back to the 1940s. In recent years, with the rising demand for the appearance of the products from consumers, application of FWAs

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Address all correspondence to Yu-Xiang Gu at guyuxiang@aliyun.com.

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in detergent becomes more and more extensive. Its function cannot be replaced by any other additives. FWAs has been listed in the industry standard of detergent raw materials in some countries (5), and almost 40% of the world's FWAs production is used in the detergent industry (6). Because there is no requirement to label FWAs in detergent labels according to the regulation, very few manufacturers state that their products contain FWAs. Compared with detergents, the application of FWAs in cosmetics is less, but it has been applied in some brands of products, e.g., Clinique (Estee Lauder, New York, NY), Estee Lauder (Estee Lauder, New York, NY), Essence Studio Nails (Irvine, CA). FWA351 and FWA184 are included in International Nomenclature Cosmetic Ingredients. FWAs may make the appearance of cosmetics more white and crystal clear. As a fashion product, pleasant color is an important factor to attract consumers to buy.

The possible toxicity of FWAs is not currently settled, with some studies suggesting that FWAs pose no risk to human, whereas other findings indicate potential for allergic and even carcinogenic effects. According to Shu's report (4), toxic effects of FWAs have not yet been observed and the toxicological information available on specific types of FWAs is rather limited, which indicates that contact with FWAs or even FWAs that migrate into food from plastic packaging containers does not represent a risk to human health. However, in other reports, FWAs have been considered to be a public health concern because of their potentially allergic and carcinogenic effect to humans, and the abuse of FWAs has aroused special concern recently (7,8). The Environmental Working Group indicated that FWAs could cause skin allergies or pruritus in sunlight, and the light-sensitive consumers should avoid contact with such substances (9). Moreover, FWAs are difficult to be degraded in terms of their special chemical stability (10), whose overuse could contribute to environmental pollution and further threaten human health as a result of their accumulation in the body.

Because information on the contents of FWAs in most cosmetics and detergent is unclear and unavailable, toxicologists cannot evaluate the possible health effects of FWAs in these products. The increasing public health concern regarding the usage of FWAs in various consumer products has stimulated our interest to investigate the content and distribution of FWAs in cosmetics and detergent, especially the most widely used distyryl-type FWAs.

In the past, determination of FWAs was performed by whiteness method (11), thin-layer chromatography (12), and direct spectrophotometric method (13). These approaches lack specificity to individual FWAs and are affected by various interfering compounds. Later, quantitation of FWAs by high-performance liquid chromatography (HPLC) has been applied to food and environmental samples (8,14–17). Recent years, combining HPLC and tandem mass spectrometry (tandem MS) with ionspray or electrospray ionization has been reported as a powerful method for determining FWAs in some materials (10,18,19). The current applications of these methods include paper, water, textile, food, *etc*. However, to our knowledge, analytical methods have been rarely reported for the determination of FWAs in cosmetics and detergent. Because quantitation of individual FWA concentration is critical in investigating the risk assessment of FWAs because of their different toxic effects, it was necessary to establish a specialized method for the FWAs in cosmetics and liquid detergent because of the varying sample composition and ensure quality control during manufacture and market supervision.

In the present study, a rapid and simple HPLC protocol is reported for the determination of five distyryl-type FWAs (FWA85, FWA210, FWA220, FWA351, and FWA353; name and structure are shown in Figure 1) in cosmetics and detergent. Diode array detector (DAD) in tandem with fluorescence detector (FLD) is employed to improve the confirmatory ability

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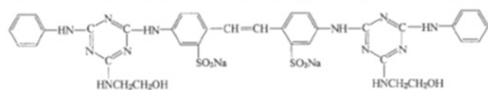
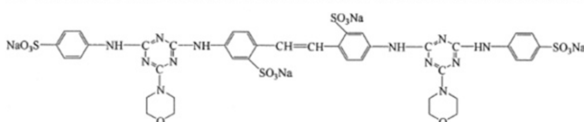
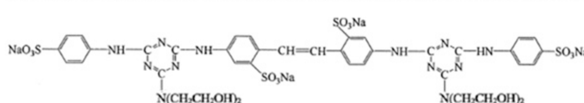
(1) Disodium 4,4'-bis[(4- anilino-6-hydroxyethylamino-1,3,5-triazin-2-y1) amino] stilbene-2,2 '-disulphonate (FWA85)



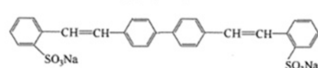
(2) Benzenesulfonic acid,2,2'-(1,2-ethenediyl) bis[5-[4-(4-morpholinyl)-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino],sodium salt (FWA210)



(3) Benzenesulfonic acid, 2,2'-(1,2-ethenediyl) bis[5-[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl) amino]-1,3,5-triazin-2-yl] amino], tetrasodium salt (FWA220)



(4) Disodium distyrylbiphenyl disulfonate (FWA351)



(5) 4,4'-bis[6-(2,5-disulfonic sodium phenylamino-4-morpholino-1,3,5-triazine-2-amino] stilbene-2,2'-disulfonic acid, sodium salt (FWA353)

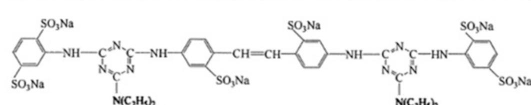


Figure 1. Name and structure of five distyryl-type fluorescent whitening agents (FWA).

of ordinary HPLC which use DAD or FLD solely. Qualification with both the ultraviolet spectral comparison (210–400 nm) obtained by DAD and fluorescence of analytes obtained by FLD would confirm the presence of FWAs more convincingly. The method is suitable for laboratories that do not have access to HPLC-tandem MS. The sensitivity and selectivity of the developed method was demonstrated to be suitable for this application.

EXPERIMENTAL

INSTRUMENTATION AND REAGENTS

HPLC method was carried out using a Waters 2695 system with DAD in tandem with FLD (Waters, Milford, MA).

FWAs (>95%) was received from Anpel Laboratory Technologies (Shanghai) Inc (Anpel, Shanghai, China). HPLC-grade solvents (acetonitrile) were purchased from Merck (Merck, Darmstadt, Germany). Reagent-grade ion-pair reagent di-*n*-hexylammonium acetate (DHAA) was got from Tokyo Chemical Industry (Tokyo Chemical Industry, Tokyo, Japan). Other reagents were purchased from Sinopharm Chemical Reagent (Sinopharm, Shanghai, China). Samples were obtained from local markets.

PREPARATION OF STANDARDS AND QUALITY CONTROL SAMPLES

The five standard FWAs (50.0 mg) were separately suspended in 90 ml water–acetonitrile solution (2:1, v/v) with ultrasonication in the dark. The solution was cooled to room

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temperature, diluted to 100 ml with 2:1 water–acetonitrile, and passed through a 0.22-μm filter. The stock solution was mixed by equal amount of these five standard solutions. Working standard solutions were obtained by diluting the stock solution to 0.10, 0.50, 2.00, 10.0, 50.0, and 100 $\mu g \cdot ml^{-1}$. All standard solutions were stored in the refrigerator in darkness to prevent the light-induced conversion of the *trans* isomers of FWAs to the *cis* isomers. Quality control samples were prepared containing each FWAs at low (5.0 $mg \cdot kg^{-1}$), medium (50.0 $mg \cdot kg^{-1}$), and high (500.0 $mg \cdot kg^{-1}$) concentrations to evaluate the accuracy, precision, and stability.

EXTRACTION OF FWAS

Cosmetics: a 1.00 g of sample was accurately weighed, treated with 8 ml of 2:1 water–acetonitrile (a small amount of quartz sand were added to emulsion, cream, lotion, and mask samples), and shaken vigorously for 1 min. The samples were sonicated for 10 min, cooled to room temperature, diluted to 10 ml with 2:1 water–acetonitrile, centrifuged at 10,000 $revolutions \cdot min^{-1}$ for 5 min, and passed through a 0.22-μm membrane filter.

Liquid detergent: A 0.20 g of sample was accurately weighed, treated with 8 ml of 2:1 water–acetonitrile, and shaken vigorously for 1 min. The samples were sonicated for 10 min, cooled to room temperature, diluted to 10 ml with 2:1 water–acetonitrile, and passed through a 0.22 μm membrane filter.

HPLC

HPLC was carried out using a Waters 2695 system and Shiseido MG C18 column (250 × 4.6 mm, 5 μm). The target analytes were separated by a gradient elution program (Table I) with the mobile phase of a mixture of acetonitrile (A) and 2 $mmol \cdot l^{-1}$ DHAA in 10 $mmol \cdot l^{-1}$ ammonium acetate (B). The column temperature was maintained at 40°C, the flow rate was 1 $ml \cdot min^{-1}$, and the injection volume was 10 μl. DAD detector was set at a compromised optimal absorption wavelength of 210–400 nm for all target FWAs. The fluorescence detection was monitored at an excitation wavelength of 350 nm and an emission wavelength of 432 nm.

The specificity of the HPLC protocol was evaluated by the analysis of a variety of cosmetics and detergent. These samples included makeup water, lotion, cream, emulsion, mask, and liquid detergent. The suppliers confirmed that the samples did not contain FWAs.

Table I
Gradient Elution Program

Time (min)	Mobile phase A: acetonitrile (%)	Mobile phase B: 2 $mmol \cdot l^{-1}$ DHAA in 10 $mmol \cdot l^{-1}$ ammonium acetate (%)
0.0	35	65
12.0	35	65
24.0	45	55
25.0	35	65
35.0	35	65

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The ultraviolet absorption spectrum from 210 to 400 nm was used for the qualitative evaluation of the analytes. Qualification of the compound peaks was identified by comparison with the retention time and the ultraviolet spectra of the standard solutions, and quantities were calculated using response factor of FLD. Figure 2 shows the ultraviolet spectrum of five FWAs standard (210–400 nm).

HPLC METHODOLOGY

The linear regression equations and the correlation coefficients were calculated by the least squares method. The limits of detection and quantization were calculated as three and 10 times the standard deviation of the baseline noise for blank extractions of samples, respectively. The intraday and interday precision were evaluated by analyzing six replicates of quality control samples at low, medium, and high concentrations. The accuracy was evaluated as the percent deviation of the mean detected concentrations from the nominal concentrations. Accuracy within ±10% of the nominal concentration and precision with relative standard deviation less than 10% were considered to be acceptable.

The recovery measurements were performed in triplicate. The recovery was determined by dividing the value obtained for the sample prepared with the added standard, by the amount added, and then multiplying by 100%. Makeup water, cream, mask, and liquid detergent were employed in the recovery studies.

The stability of quality control samples was assessed by analyzing samples stored for 1 week at 4°C and stored for 24 h at room temperature. The samples were considered to be stable when the deviation from the nominal concentration was within ±10.0%.

RESULTS AND DISCUSSION

EXTRACTION

Most of the distyryl-type FWAs were easy to dissolve in water; hence, four extraction solvents, including water, water–acetonitrile (2:1, v/v), water–acetonitrile (1:2, v/v), and acetonitrile were selected to optimize the extraction conditions. Meanwhile, effects of different ultrasonic time (10, 20, and 30 min) on the extraction efficiency of target analytes were also investigated.

Compared with extraction with water, lower matrix interference was obtained using water–acetonitrile (2:1, v/v). Because the solubility of FWAs in acetonitrile was inferior to water, the recovery values decreased for excessively high concentration of acetonitrile in extraction solvent (data not shown). Quartz sand was helpful for demulsification to extract the target analytes in emulsion, cream, lotion, and mask samples. Results found that the recoveries of the FWAs approached equilibrium when the sample was ultrasonicated for 10–30 min. Hence, ultrasonication for 10 min was selected in the next experiment.

HPLC

Compared with DAD, FLD had higher sensitivity and no response to the substance without fluorescence characteristics. Thus, using FLD could contribute to reduce the interference

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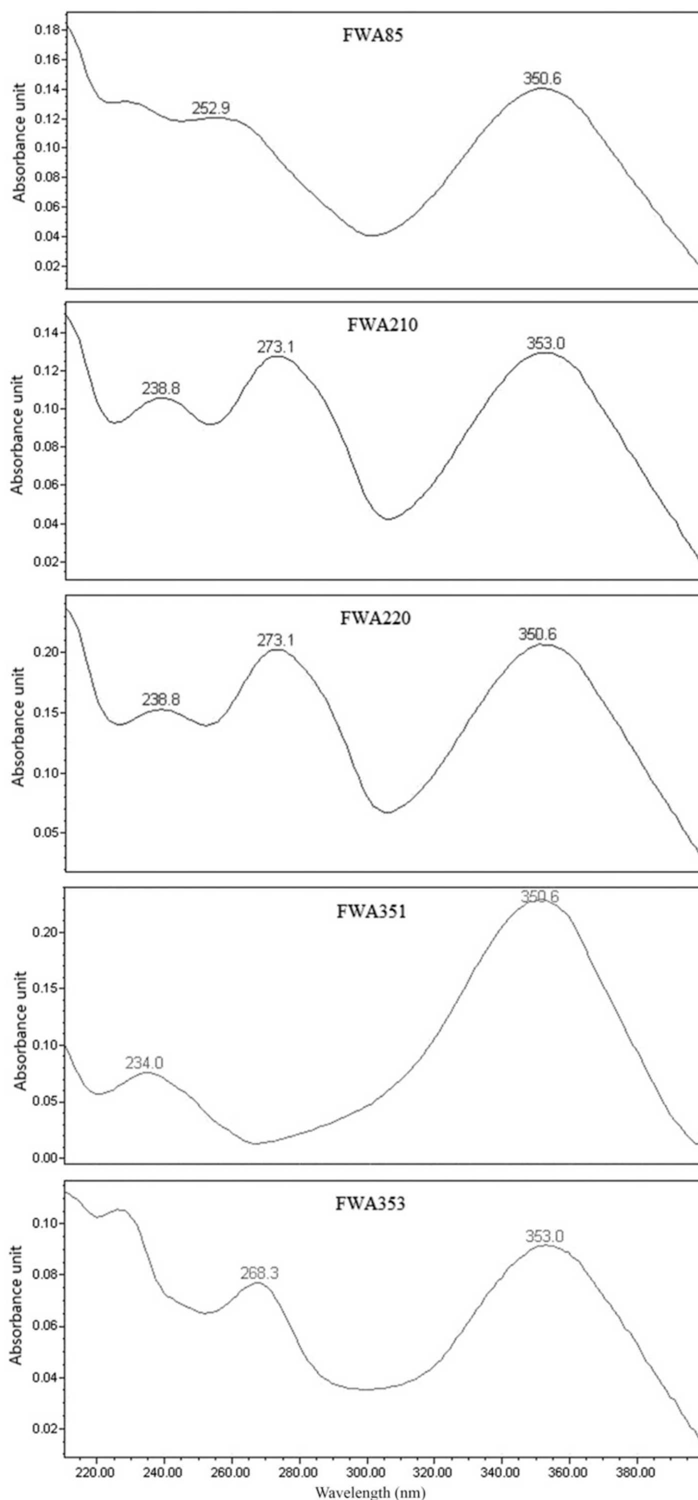

Figure 2. Ultraviolet spectrum of five distyryl-type fluorescent whitening agents (FWA) standard.

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of the matrix. Figure 3 shows that some impurities which had ultraviolet absorption at 350 nm could not interfere in the determination of FWAs in samples by FLD. However, the retention time was the solely qualitative basis of FLD method, whereas both retention time and ultraviolet spectrum of analytes were the qualitative basis of DAD method. Therefore, these two detectors were combined to use their respective advantages. If impurity peaks were present near the retention time of the analytes in the chromatogram of FLD, they might be distinguished by comparing the ultraviolet spectrum using the DAD. The method was suitable for laboratories that did not have access to HPLC-tandem MS. Compared with ordinary HPLC that use DAD or FLD sole, the confirmatory ability of this method was improved. Moreover, the limits of detection and quantization were close to HPLC-tandem MS method.

The distyryl-type FWAs in aqueous solution were in the form of anion, the molecular structure of analyte steric showed weak retention and could not be completely separated on a reversed-phase chromatographic column. Hence, it was necessary to use ion-pairing reagent to enhance the binding ability of the object to be measured and the stationary phase. To use the mobile phase in the further research of HPLC-tandem MS method with slight improvement, a suitable ion-pairing reagent was needed. Ordinary ion-pairing reagents suppressed the ESI signal and cause contamination of the ion source, especially nonvolatile tetraalkylammonium salts (20,21). Volatile di- and trialkylammonium acetates provide similar separation selectivity to that of tetraalkylammonium salts but greatly reduce ESI signal suppression. Among them, DHAA was compatible with MS detection, increasing

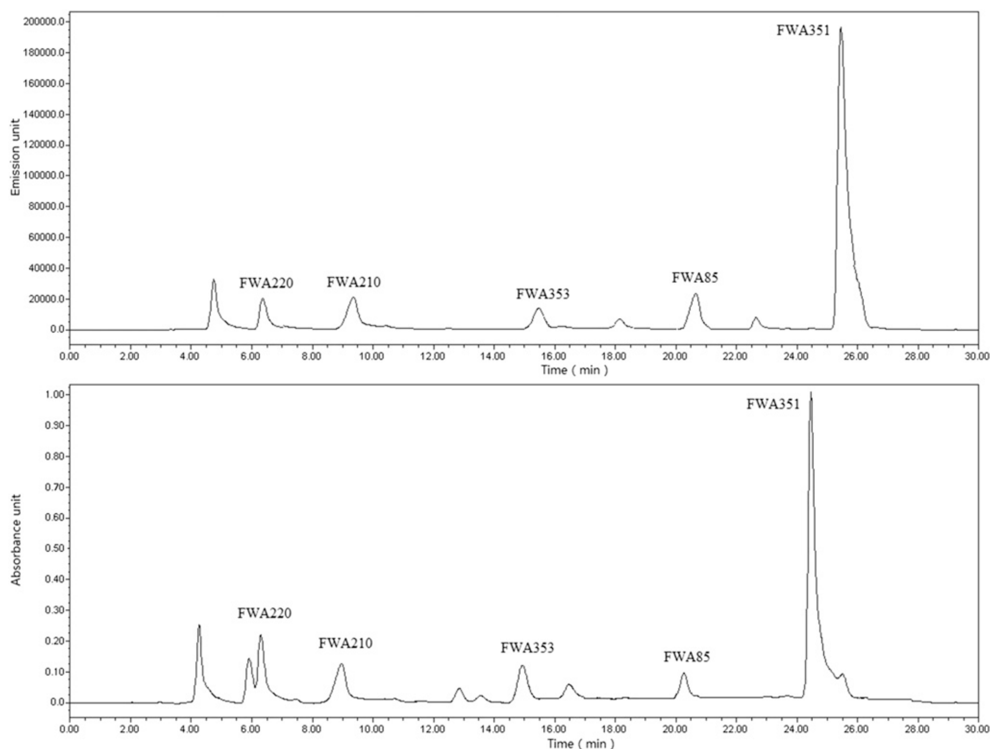

Figure 3. Chromatography of cosmetic sample which contained five fluorescent whitening agent (FWA) standards by fluorescence detector (upper) and diode array detector (below).

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the retention and improving the separation of FWAs. Thus, DHAA was selected in the present work.

Because the ion-pairing reagent caused damage to the chromatographic column, concentration of acetonitrile in the mobile phase was decreased to reduce the use of DHAA. Various concentrations of DHAA (1–5 $mmol \cdot l^{-1}$, in the ammonium acetate solution) and acetonitrile (30–40%, in the mobile phase) were evaluated to determine the mobile phase composition that offers the highest signal-to-noise (S/N) ratio and sufficient resolution for the FWAs. The highest S/N ratio and good separation of these five analytes were achieved with 2 $mmol \cdot l^{-1}$ DHAA as the ion-pairing reagent to form neutral ion pairs, which promote the hydrophobic interaction between the analytes and the C18 stationary phase. Under this condition, the best concentration of acetonitrile in the mobile phase was 35%.

Moreover, the ratio of ammonium acetate, which was commonly used in the HPLC analysis for improving separation, was optimized. Lower concentrations of ammonium acetate produced excessively wide peaks and long retention times, whereas higher concentrations of ammonium acetate led to insufficient separation of target compounds and impurities. Hence, the best composition of ammonium acetate was 10 $mmol \cdot l^{-1}$.

After optimization, the initial mobile phase was determined to be a mixture of 35% acetonitrile and 65% 2 $mmol \cdot l^{-1}$ DHAA in 10 $mmol \cdot l^{-1}$ ammonium acetate. However, the retention time of FWA351 was too long in this situation. Thus, a gradient elution program was adopted. The concentration of acetonitrile was linearly increased to 45% from 12 to 24 min, and then decreased back to 35% from 24 to 25 min, at last, maintained the concentration for 10 min.

The effects of three C18 columns, including Shiseido MG C18 (Shiseido, Tokyo, Japan), Merck RP18 column (Merck, Darmstadt, Germany), and Agilent SB C18 (Agilent, Palo Alto, CA), on the separation of the five target FWAs were investigated. Chromatographic peaks of some FWAs were tailed in Merck RP18 column and Agilent SB C18 column, whereas good shape of the peak was observed using Shiseido MG C18 column.

Ionic surfactant, a commonly used component in liquid detergent, might interact with ion-pairing reagents in the mobile phase and led to the weak combination of the FWAs and ion-pairing reagents. Because of this, the retention time of some analytes in detergent samples became shorter than the retention time of the same FWAs in standard solutions.

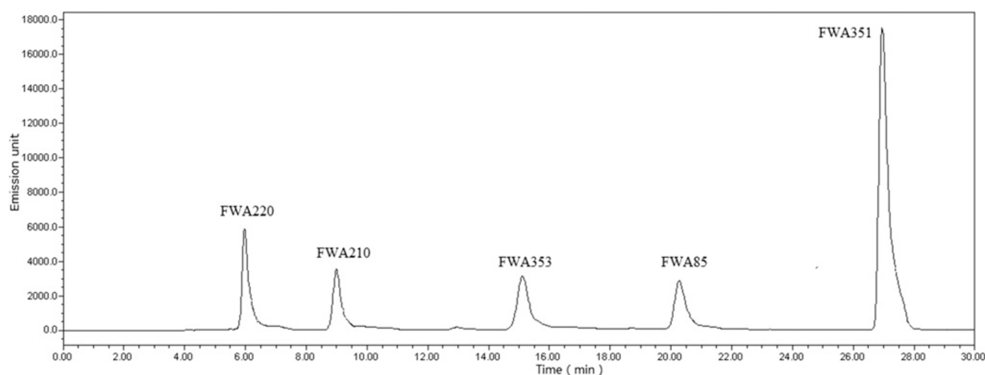

Figure 4. Chromatography of standard solutions which contained five fluorescent whitening agents (FWA) standards.

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Table II
Recovery Tests

Sample	FWAs	Sample prepared with the added FWAs standard ($mg{\cdot}kg^{-1}$)	Analysis results ($mg{\cdot}kg^{-1}$)	Mean recovery (%)
Liquid detergent	85	0.5	0.440 ± 0.025	88.0 ± 5.0
	210		0.462 ± 0.020	92.4 ± 4.0
	220		0.451 ± 0.024	90.2 ± 4.8
	351		0.485 ± 0.017	97.0 ± 3.4
	353		0.410 ± 0.015	82.0 ± 3.0
	85	5	4.19 ± 0.23	83.7 ± 4.6
	210		4.47 ± 0.19	89.3 ± 3.8
	220		4.31 ± 0.16	86.1 ± 3.2
	351		4.77 ± 0.34	95.4 ± 6.8
	353		4.26 ± 0.20	85.2 ± 4.0
	85	50	45.0 ± 2.8	89.9 ± 5.6
	210		46.6 ± 2.3	93.1 ± 4.6
	220		45.4 ± 1.4	90.8 ± 2.8
	351		48.0 ± 1.1	96.0 ± 2.2
	353		43.0 ± 1.9	85.9 ± 3.8
Makeup water	85	0.5	0.429 ± 0.033	85.8 ± 6.6
	210		0.440 ± 0.029	88.0 ± 5.8
	220		0.451 ± 0.030	90.2 ± 6.0
	351		0.407 ± 0.024	81.4 ± 4.8
	353		0.416 ± 0.020	83.2 ± 4.0
	85	5	4.43 ± 0.25	88.6 ± 5.0
	210		4.41 ± 0.18	88.1 ± 3.6
	220		4.43 ± 0.21	88.6 ± 4.2
	351		4.61 ± 0.32	92.1 ± 6.4
	353		4.27 ± 0.29	85.4 ± 5.8
	85	50	46.5 ± 2.7	92.9 ± 5.4
	210		47.7 ± 2.4	95.3 ± 4.8
	220		47.8 ± 1.5	95.5 ± 3.0
	351		51.7 ± 1.2	103.3 ± 2.4
	353		49.9 ± 1.8	99.7 ± 3.6
Mask	85	0.5	0.431 ± 0.029	86.2 ± 5.8
	210		0.406 ± 0.025	81.2 ± 5.0
	220		0.410 ± 0.028	82.0 ± 5.6
	351		0.422 ± 0.017	84.4 ± 3.4
	353		0.507 ± 0.030	101.4 ± 6.0
	85	5	4.41 ± 0.25	88.2 ± 5.0
	210		4.36 ± 0.21	87.2 ± 4.2
	220		4.53 ± 0.23	90.6 ± 4.6
	351		4.92 ± 0.12	98.3 ± 2.4
	353		4.37 ± 0.20	87.4 ± 4.0
	85	50	41.2 ± 2.1	82.3 ± 4.2
	210		44.8 ± 1.0	89.5 ± 2.0
	220		46.2 ± 1.3	92.3 ± 2.6
	351		48.4 ± 1.5	96.8 ± 3
	353		48.2 ± 2.1	96.3 ± 4.2

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Table II
Continued

Sample	FWAs	Sample prepared with the added FWAs standard ($mg{\cdot}kg^{-1}$)	Analysis results ($mg{\cdot}kg^{-1}$)	Mean recovery (%)
Cream	85	0.5	0.440 ± 0.027	88.0 ± 5.4
	210		0.412 ± 0.033	82.4 ± 6.6
	220		0.452 ± 0.028	90.4 ± 5.6
	351		0.505 ± 0.020	101.0 ± 4.0
	353		0.463 ± 0.022	92.6 ± 4.4
	85	5	4.04 ± 0.26	80.7 ± 5.2
	210		4.22 ± 0.23	84.3 ± 4.6
	220		4.30 ± 0.18	86.0 ± 3.6
	351		4.55 ± 0.22	91.0 ± 4.4
	353		4.64 ± 0.12	92.7 ± 2.4
	85	50	44.6 ± 2.9	89.2 ± 5.8
	210		44.4 ± 1.5	88.7 ± 3.0
	220		45.0 ± 1.6	90.0 ± 3.2
	351		47.9 ± 2.3	95.8 ± 4.6
	353		44.6 ± 2.0	89.2 ± 4.0

This might lead to the wrong results of determination. Although the problem could be solved by standard addition method, the method was rather tedious, which was not suitable to batch tests. The situation could be effectively improved by decreasing the amount of sample from 1.0 to 0.2 g. In this case, the retention time of FWAs in standard solutions were consistent with the retention time of the same FWAs in liquid detergent samples.

The optimized chromatographic conditions provided a good separation of five FWAs in an appropriate analysis time. The developed method was adopted to determine the target analytes in a variety of makeup water, lotion, cream, emulsion, mask, and liquid detergent samples without FWAs. Results demonstrated that impurity compositions in the samples had no interferential effects on the determination of the five FWAs, indicating that the specificity of the developed method was favorable. A typical chromatogram of five FWAs standards is shown in Figure 4.

ANALYTICAL FIGURES OF MERIT

Linear responses to FWAs concentration were obtained from 0.100 to 100.0 $\mu g{\cdot}ml^{-1}$. The correlation coefficients were 0.9988–0.9995. The limits of detection were 0.1, 0.1, 0.05, 0.01, and 0.1 $mg{\cdot}kg^{-1}$ for FWA85, 210, 220, 351, and 353, respectively. The limits of quantification were 0.4, 0.4, 0.2, 0.04, and 0.4 $mg{\cdot}kg^{-1}$ for FWA85, 210, 220, 351, and 353, respectively. The intraday and interday precisions were from 3.01% to 6.76% and 3.03–7.21%. The accuracy of the method was from −5.31% to +5.47%. The results demonstrated that the procedure provided acceptable accuracy and precision. The recovery was from 80.7% to 103.3% (Table II). These satisfactory values indicated that quantification by external calibration might be employed. The target analytes were stable for 24 h at room temperature and for 1 week at 4°C in the dark.

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Table III
Content of FWAs in Nine Positive Real Samples

Sample	FWAs	Content of FWAs ($mg \cdot kg^{-1}$)
Plant laundry liquid detergent	FWA351	231
White photoflo	FWA351	1,130
Quick effect liquid detergent	FWA351	368
Full-care liquid detergent	FWA351	187
Laundry liquid detergent	FWA351	203
Brilliant color and white photoflo	FWA351	1,105
Liquid detergent	FWA85	400
Laundry liquid detergent	FWA351	194
Revitalizing antiwrinkle eye cream	FWA351	19.4

ANALYSIS OF COSMETICS AND DETERGENT

The protocol was validated on the basis of precision, accuracy, stability, and recovery, demonstrating its suitability for the analysis of cosmetics and liquid detergent. The method was adopted to analyze 50 commercial products (35 cosmetics and 15 liquid detergents) from local markets for FWAs. Results indicated that FWA351 and FWA85 were detected in eight liquid detergent samples (Table III), whose contents were determined to be in the range of 187–1,130 $mg \cdot kg^{-1}$. The chromatogram for the analysis of FWA351 in sample "brilliant color and white photoflo" is shown in Figure 5. It was revealed that FWA351 was the most commonly used FWA in the detergent productions, which coincided with the market research. Because of the increasing doubts about the safety of FWAs in recent years, the use of FWAs in cosmetics became few. Only one

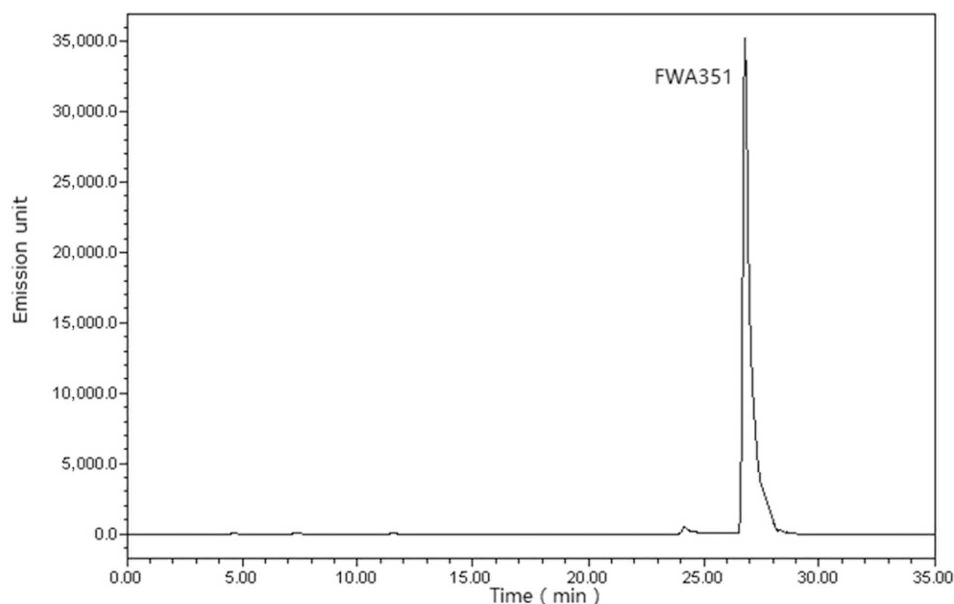

Figure 5. Chromatography of sample "brilliant color and white photoflo" which contained 1,105 $mg \cdot kg^{-1}$ FWA351.

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sample was detected with FWA351 at 19.4 mg·kg^{-1}. These results suggested that further study is necessary to evaluate the risk of FWAs in cosmetics and liquid detergents.

CONCLUSIONS

Based on the technology of ion-pairing chromatography, a simple and sensitive analytical method, using the HPLC-DAD-FLD, was developed and validated for the simultaneous determination of five distyryl-type FWAs in cosmetics and liquid detergent. The limits of detection were from 0.01 to 0.1 mg·kg^{-1}, and the limits of quantification were from 0.04 to 0.4 mg·kg^{-1}. The recovery values were between 80.7% and 103.3%. The results in this study revealed that FWA85 and FWA351 were present in various commercial products. The developed method could provide scientific technical support for further sources of FWA pollution and the risk assessment.

ACKNOWLEDGMENTS

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