A System for Determining Optical Brighteners in Laundry Detergents by TLC and HPLC

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Twenty-three optical brighteners have been separated on a thin-layer chromatographic (TLC) system and a high-performance liquid chromatographic (HPLC) system. These systems can be used to identify and quantitate optical brighteners in laundry detergents. The TLC system uses four solvent-absorbent combinations. The HPLC system uses a C_8 column and a binary solvent gradient program to separate the optical brighteners.

KEY WORDS: Laundry detergents, optical brighteners, thin-layer chromatography.

Optical brighteners are added to laundry detergents to enhance the perceived whiteness of a fabric. The optical brighteners absorb radiation in the ultraviolet (UV) region and emit light in the visible region (1). This makes the statement "whiter-than-white," in fact, true.

The analysis of optical brighteners has been approached from several different aspects. Theidel and Schmitz (2) used four thin-layer chromatography (TLC) systems to differentiate sixteen optical brighteners that are primarily sold in Europe. In 1974, Schulze, Polaro and Stensby (3) used four TLC systems to separate ten optical brighteners commonly used in laundry detergents. Lloyd (4) used TLC to identify nine optical brighteners that can be extracted from fibers and detergents. Lepri, Desideri and Coas (5) studied the effect of various reverse-phase absorbents on the thin-layer chromatography of twenty optical brighteners.

High-performance liquid chromatography (HPLC) was first applied to optical brighteners in 1976. Seven optical brighteners were separated on a silica column with an isocratic solvent system (6). McPherson and Omelczenko (7) used two reversed-phase isocratic HPLC systems to baseline-separate eleven optical brighteners. Workers at Ciba-Geigy Corp. (Greensboro, NC) separated six optical brighteners on a C_8 reverse-phase column with 0.01 M tetrabutylammonium phosphate solution at pH 7/tetrahydrofuran/acetonitrile (52:2.4:45.6) (8).

Twenty-nine fluorescent whitening agents are listed in *McCutcheon's Functional Materials* (9). Twenty-three of the optical brighteners were selected to provide a comprehensive collection that previous work has not addressed. This paper presents a system for identifying and quantitating all twenty-three optical brighteners in laundry detergent formulations by TLC and HPLC.

EXPERIMENTAL PROCEDURES

Materials. The optical brighteners were obtained from Ciba-Geigy Corp., Eastern Color and Chemical Co. (Providence, RI), Mobay Chemical Co. (Union, NJ), Crompton and Knowles Corp. (Gibraltar, PA), Sandoz Chemicals (Charlotte, NC), Eastman Chemical Products, Inc. (Kingsport, TN), American Cyanamid Co. (Wayne, NJ) and Continental Chemical Co. (Clifton, NJ).

Tinopal BLS-X, Tinopal AMS, Tinopal CBS-X, Tinopal 5BM, Tinopal LPW, Tinopal RBS, Tinopal DCS and Tinopal 4264 are registered trade names of Ciba-Geigy Corp. ECCO Brite RB-6, ECCO White Nylon FW-5, ECCO White C-704, ECCO Polyester 525-V and ECCO White OP are registered trade names of Eastern Color and Chemical Co. Intrawite TPA, Intrawite WGS, Intrawite EHN, Intrawite ARL, Intrawite ERN, Intrawite EBF, Intrawite CF and Intrawite CK are registered trade names of Mobay Chemical Co. Phorwite RKH 766, Phorwite FBW and Phorwite BHC 766 are registered trade names of Crompton and Knowles Corp. Arctic White GT, Arctic White TX and Arctic White SOL are registered trade names of Sandoz Chemicals.

HPLC-grade methanol, acetonitrile, chloroform, hexane, methylene chloride and isopropanol were purchased from Fisher Scientific (Fairlawn, NJ). Tetrabutylammonium bromide and tetraethylene glycol dimethyl ether were purchased from Aldrich Chemical Co. (Milwaukee, WI). USP-grade ethanol was purchased from Quantum Chemical Corp. (Cincinnati, OH). Distilled water was passed through a Universal Ion X-Changer followed by a Research Ion X-changer (Cole-Parmer Instrument Co., Chicago, IL) to give 15 Mohms/cm^3 water.

Thin-layer chromatography instrumentation. KC18 F reversed-phase and CS5 Multi-K $KC_{18}F/K5F$ TLC plates were purchased from Whatman Chemical Separations, Inc. (Clifton, NJ). The TLC plates were either 10 × 10 cm or 20 × 20 cm. The TLC apparatus consisted of a rectangular glass tank lined with filter paper saturated with about 100 mL of solvent.

Disposable micropipettes (3-μL) (Drummond Scientific Co., Broomall, PA) were used to transfer the sample solutions to the TLC plate. The spots were developed by exposing the dried plates to long-wave UV radiation (330 nm).

TLC sample preparation. The detergent sample (0.2 g) was dissolved/dispersed in 2 mL of methanol. The sample solution (3 μL) was spotted on the TLC plate with a spot diameter of 2 mm.

High-performance liquid chromatography instrumentation. A Varian 5000 liquid chromatograph (Varian Associates, Sugarland, TX) equipped with a Varian UV-50 UV/Vis detector set at 330 nm was used in this study. A Spectra-Physics SP4200 integrator (Spectra-Physics, Piscataway, NJ) was used to process the data. A Spherisorb C_8 250 mm × 4.6 mm was used for the HPLC separations (Alltech Associates, Deerfield, IL). The particle size is 5 microns.

The solvents for this HPLC separation are as follows: Solvent A = acetonitrile/methanol/water 20:40:40 with 0.05 M tetrabutylammonium bromide, Solvent B = methylene chloride/isopropanol 10:90 with 0.01 M tetrabutylammonium bromide.

The solvent program is from 0 to 5 min 100% Solvent A at 1 mL/min; 5 to 25 min, Solvent B increasing from 0 to 34%; 25 to 35 min, Solvent B increasing from 34% to 40%; 35 to 45 min, Solvent B increasing from 40% to 90%; and 45 to 50 min hold at 90% Solvent B. Reequili-

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brate the column by increasing Solvent A from 10% to 100% over a ten-minute period.

HPLC standard preparation. Stock standards (1000 ppm) of the optical brighteners were dissolved in 5 mL of tetraethylene glycol dimethyl ether and 5 mL isopropanol in a 50-mL volumetric flask. Sonication was usually required to dissolve the optical brighteners. The stock standard solution was diluted to the mark with Solvent A described above. A 50-ppm working standard was made by diluting the stock standard 1/20 with Solvent A. The sample was then stored in the dark.

HPLC sample preparation. The laundry detergents were dissolved on a 5% weight basis in water and filtered through a 10-μm filter if necessary.

RESULTS AND DISCUSSION

This system for determining optical brighteners in laundry detergents uses TLC as an initial qualitative screen and HPLC for confirmation and quantitation.

Generally, careful selection of the TLC systems listed in Table 1 will give enough separation to identify the optical brightener(s) present in the selected laundry detergent.

Table 1 lists the TLC system that will uniquely identify the specified optical brightener. Four TLC systems are needed to separate these 23 optical brighteners. When two R_f values are given for an optical brightener, this indicates two spots were observed.

Figure 1 is an example of the optical brighteners present in some commercial laundry detergents. The optical brighteners suspected to be present in these detergents are run as standards.

Occasionally, a detergent is so heavily formulated that the chromatography of the optical brightener in the sample is poor. Two-dimensional thin-layer chromatography can be employed to improve the separation and hence aid in identification, as exemplified in Figure 2. The sample is spotted on a KC18 F reverse-phase TLC plate and run with ethanol/water 75:25 as the solvent. The solvent front is only allowed to rise 7 cm on a 10-cm TLC plate. The plate is air-dried and rotated 90 degrees and run in one of the above TLC systems. As can be seen in Figure 2, the chromatography degrades somewhat due to broadening during elution with the first solvent, but identification of the optical brightener is still possible.

HPLC can be used to confirm and quantitate the TLC

TABLE 1

R_f Values of Selected Optical Brighteners

Optical brightener	System A[a]	System B	System C	System D	Preferred system
Tinopal BLS-X[b]	0.45	1	—	—	A
Tinopal AMS	0.58	1	—	—	A
Tinopal CBS-X	0.46, 0.57	1	—	—	A
Tinopal 5BM, ECCO Brite RB-6, Intrawite TPA, ECCO White Nylon FW-5	0.58	0.89	1	1	A
Tinopal LPW	0.81	1	—	—	A
Tinopal RBS	0.03	0.68	0.87	0.82	B
Tinopal DCS	1	1	—	0.21, 0.31, 0.46	D
Tinopal 4264	0, 0.05	0, 0.11	0.01	—	C
Phorwite RKH 766	0.73	1	—	—	A
Phorwite FBW	—	0.51	0.78	—	B
Phorwite BHC 766	0.41, 0.61	1	—	—	A
Arctic White GT	1	1	—	0.49	D
Arctic White TX	0.94	1	—	0.38	D
Arctic White SOL, ECCO White C-704, Calcofluor; White RWP, Conoflor 900, Intrawite WGS	—	0.38	0.70	—	B
Leucophor BMB	1	1	—	0.44	D
Leucophor EGM	0	0.05	0.44	—	C
Eastobrite OB-1	0	0	0.38	—	C
Intrawite EHN	0	0.06, 0.14	0.48, 0.55	—	C
Intrawite ARL	0.05	0.11	0.30	—	C
Intrawite ERN, ECCO Polyester 525-V	0	0.11, 0.19	0.50	0.85	C
Intrawite EBF, ECCO White OP	0	0.10	0.35, 0.50	0.85	C
Intrawite CF	0.79	0.92	—	—	A
Intrawite CK	1	1	—	0.46, 0.51, 0.63	D

[a] TLC System A = acetonitrile/methanol/water 20:40:40 with 0.01 M tetrabutylammonium bromide. A TLC plate coated with KC18 F reversed-phase absorbent is used. TLC System B = acetonitrile/methanol/water 14.5:63:22 with 0.05 M $(NH_4)_2HPO_4$. A TLC plate coated with KC18 F reverse-phase absorbent is used. TLC System C = methanol with 0.01 M tetrabutylammonium bromide. A TLC plate coated with KC18 F reversed-phase absorbent is used. TLC System D = methanol/chloroform/hexane 65:25:10 with 0.01 M tetrabutylammonium bromide and pH adjusted to 1.5. A TLC plate coated with Silica Gel G absorbent is used.

[b] All of the trade names in first column are registered trademarks.

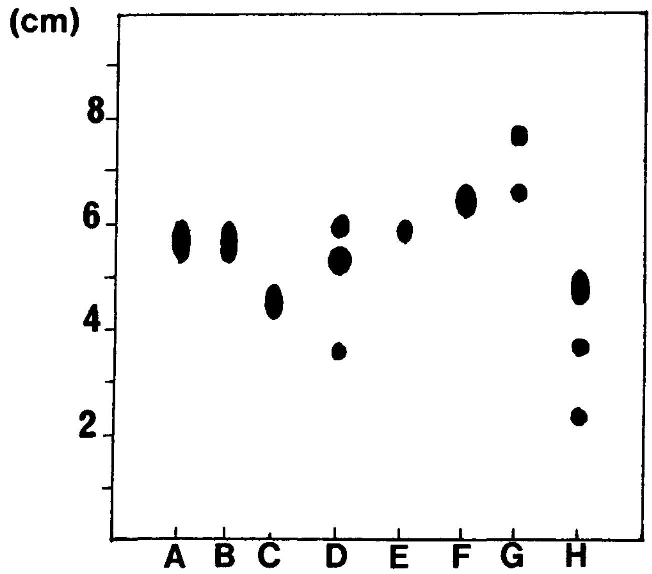

FIG. 1. TLC of optical brighteners and detergents. A, detergent A; B, detergent B; C, Phorwite BHC 766; D, Tinopal CBS; E, Tinopal 5BM; F, Phorwite RKH 766; G, Intrawite CF; and H, detergent C. TLC System: acetonitrile/methanol/water 20:40:40 with 0.01 M tetrabutylammonium bromide. A TLC plate coated with KC18 reverse-phase is used.

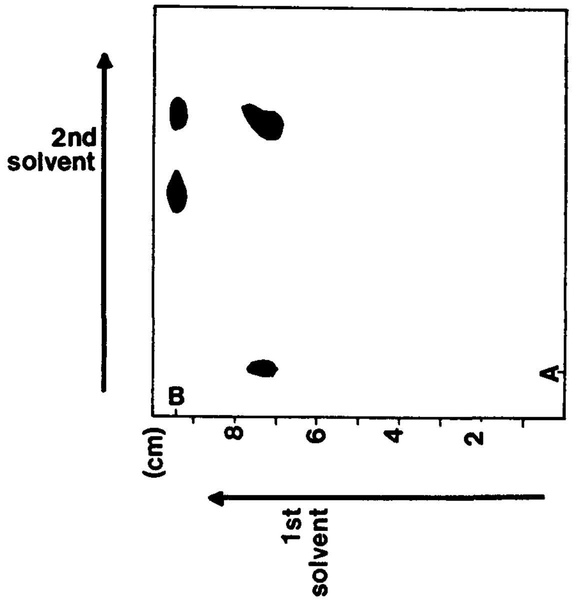

FIG. 2. Two-dimensional resolution of an optical brightener in a commercial detergent. A, 300 μg detergent D; B, Tinopal AMS and Tinopal LPW. First solvent: ethanol/water 75:25; second solvent: acetonitrile/methanol/water 20:40:40 with 0.01 M tetrabutylammonium bromide. The TLC plate is KC18 F reverse-phase.

TABLE 2

Retention Times of Selected Optical Brighteners

Optical brightener	Absolute retention time (min)	Relative retention time (Arctic White TX = 1.00)
Tinopal BLS-X	21.97	6.60
Tinopal AMS	21.20, 23.50	7.29, 8.08
Tinopal ÇBS-X	21.54	8.09
Tinopal 5BM, ECCO Brite RB-6, Intrawite TPA, ECCO White Nylon FW-5	19.66	5.90
Tinopal LPW	11.62	3.50
Tinopal RBS	23.53, 24.21	8.10, 8.40
Tinopal DCS	5.87	1.80
Tinopal 4264	7.63	2.50
Phorwite RKH 766	11.06, 15.2	3.40, 4.70
Phorwite FBW	7.57	2.40
Phorwite BHC	22.68	8.00
Arctic White GT	7.83	2.50
Arctic White TX	2.91	1.00
Arctic White SOL, ECCO White C-704, Calcofluor White RWP, Conoflor 900, Intrawite WGS	6.60	2.50
Arctic White DML	20.90, 22.00	7.90, 8.30
Arctic White MSO	20.51, 21.68	7.05, 7.45
Leucophor BMB	4.22	1.44
Leucophor EGM	27.11	8.20
Eastobrite OB-1	—	—
Intrawite EHN	21.03, 26.11	6.90, 8.60
Intrawite ARL	4.88	1.50
Intrawite ERN, ECCO Polyester 525-V	21.80	7.00
Intrawite EBF, ECCO White OP	22.56, 23.28	7.50, 7.70
Intrawite CF	13.00, 15.30	4.30, 5.10
Intrawite CK	6.06, 7.55	2.10, 2.60

results. Generally, HPLC is used to confirm the identity of the optical brighteners and can be used to quantitate the amount of optical brightener that may be present in a laundry detergent formulation. Optical brighteners are usually present in laundry detergents at the 0.5% level (10).

Table 2 lists the absolute and relative retention times (compared to Arctic White TX) for the solvent program listed in the Experimental Procedures section.

Figures 3–5 are examples of the type of high-performance liquid chromatography that can be expected for optical brighteners. Because each optical brightener has multiple peaks, the chromatograms of the optical brighteners are shown separately.

Figure 6 is a chromatogram of a 1% solution of Detergent A. The other compounds in laundry detergents have a lower extinction coefficient than optical brighteners. This makes detection of optical brighteners in laundry detergents an easy task. The peak at 20 min is the optical brightener, Tinopal 5BM.

This is confirmed by TLC and coinjection of a solution to Tinopal 5BM and a 1% solution of Detergent A. It is important to confirm the identity of the optical brightener by coinjection, as the other components in the detergent can slightly shift the retention time of the optical brightener.

Of these two methods, TLC is faster and can scan for many possible optical brighteners in a sample. HPLC is used as a confirmatory method and can provide quantitative information.

Table 3 is a list of common laundry detergents with the type and amount of optical brightener(s) present. The laundry detergents were first scanned by TLC to determine which optical brighteners are present. HPLC was then used to quantitate the optical brighteners and confirm identity.

In this way, laundry detergents can be examined for the types and quantity of optical brighteners present.

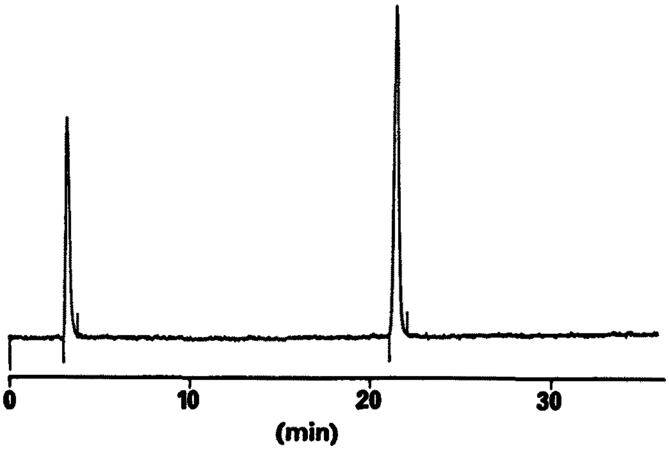

FIG. 3. HPLC of Tinopal CBS-X with a Spherisorb C_8 column and the binary solvent program described in the Experimental Procedures section.

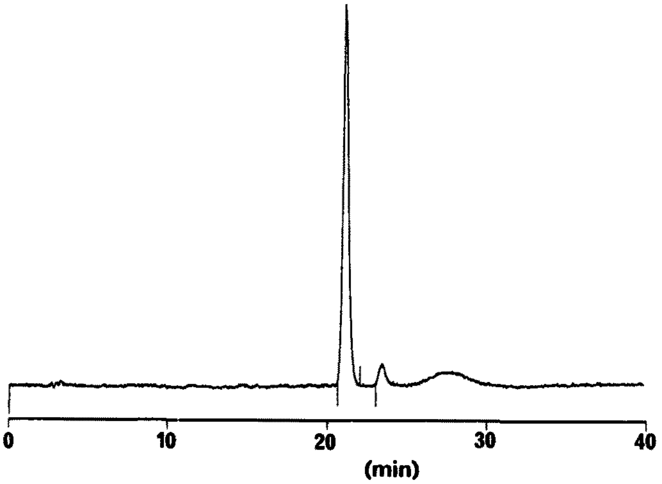

FIG. 4. HPLC of Tinopal AMS with a Spherisorb C_8 column and the binary solvent program described in the Experimental Procedures section.

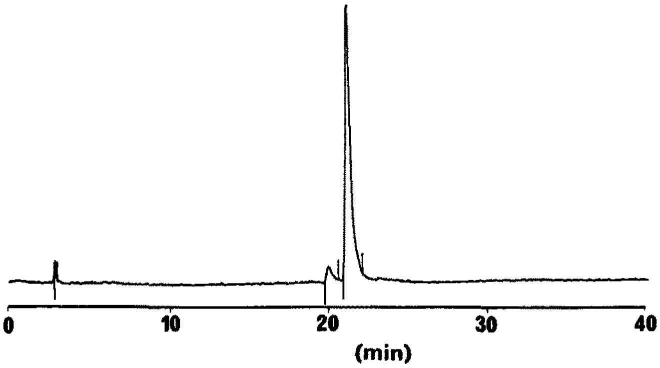

FIG. 5. HPLC of Arctic White MSO with a Spherisorb C_8 column and the binary solvent program described in the Experimental Procedures section.

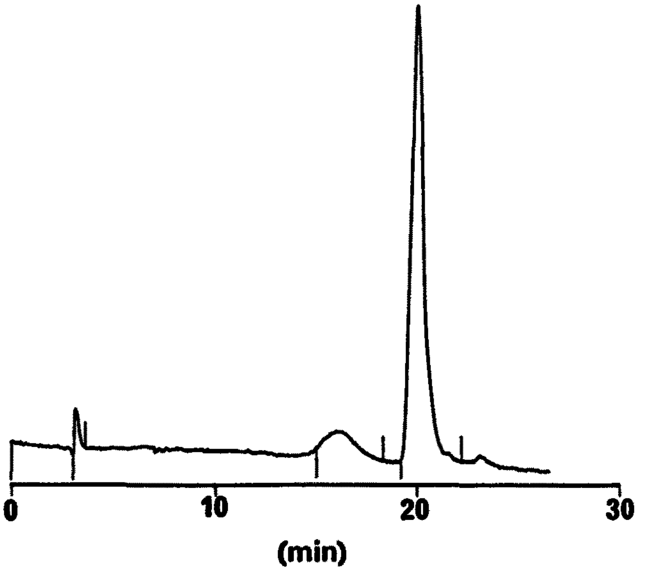

FIG. 6. Solution (1%) of detergent A detergent showing the presence of Tinopal 5BM at 20 min.

TABLE 3

Optical Brighteners in Laundry Detergents

Sample	Optical brightener	Amount
Detergent A	Tinopal 5BM	0.15%
Detergent B	Tinopal 5BM	0.05%
Detergent C	Tinopal AMS	0.07%
Detergent D	Tinopal AMS	0.21%
Detergent E	Phorwite BHC 766	0.04%
	Tinopal 5BM	0.11%
Detergent F	Tinopal 5BM	0.11%
Detergent G	Tinopal RBS	0.08%
Detergent H	Tinopal AMS	0.04%
	Tinopal LPW	0.16%
Detergent I	Tinopal AMS	0.10%
	Tinopal LPW	0.52%
Detergent J	Tinopal RBS	0.03%

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