The Determination of Optical Brighteners in Laundry Detergents by Reverse Phase and Ion Pair High Performance Liquid Chromatography

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ABSTRACT

Eleven optical brighteners have been qualitatively and quantitatively determined using C_{18}, C_8, or C_2 reverse phase high performance liquid chromatography (HPLC) columns. Comparable results also were obtained using radially compressed reverse phase HPLC cartridges. Mobile phases consist of acetonitrile and methanol in water with 0.05 M phosphate buffer. Quaternary ammonium salts also are added to the mobile phase for ion pair formation. Ultraviolet (UV) detection at 340 nm gives more than adequate sensitivity for brighteners formulated between 0.05 and 2.0%. Sample preparation is simple and all components can be eluted within 15 min. Powdered and liquid detergents, fabric softeners, and bleach boosters have been routinely analyzed and results closely agree with those obtained using thin layer chromatography and densitometry.

INTRODUCTION

Until recently the method which best suited our needs for separation and quantitation of optical brighteners in laundry products was an adaptation of the Schulze, et. al. (1) thin layer chromatography (TLC) method. Their procedure involves a preliminary TLC separation followed by quantitation on a fluorescence spectrophotometer equipped with a TLC plate scanning accessory. With a few modifications to their methods, at least 11 optical brighteners could be separated and quantitated adequately. However, the high cost of brightener raw materials forced us to look toward faster, more precise and accurate ways to monitor their presence. High performance liquid chromatography (HPLC) was the obvious choice and a literature search revealed Kirkpatrick's papers (2,3) which are adaptations of the Schulze TLC paper. Because the elution times are longer than we prefer and the mobile phase consists of less than desirable components on a safety basis, our efforts turned toward reverse phase separation which is faster and results in longer column life than silica. Figure 1 lists the brighteners which will be discussed in this paper.

EXPERIMENTAL PROCEDURES

Instrumentation

The analyses were performed with a Waters M6000A solvent delivery system and 440 ultraviolet (UV) detector fitted with a 340 nm filter (Waters Associates, Milford, MA). A Schoeffel instruments 770 variable wavelength UV detector (Kratos, Westwood, NJ) was also used for specific wavelength selections. Injections were made with a Rheodyne 7125 syringe injector (Rainin Inst., Woburn, MA) fitted with a 20 µl loop. The analytical columns used were Zorbax ODS and C_8 (Dupont Instruments, Wilmington, DE), EM Reagents Hibar—II LiChrosorb RP-2 (Applied Science Laboratories, State College, PA), and the Waters RCM-100 radial compression module fitted with a radial-PAK A C_{18} cartridge. These columns were preceded by a guard column containing pellicular C_{18} or CN packing materials depending on which analytical column was in use at the time.

Materials

J.T. Baker HPLC grade methanol and acetonitrile were purchased from Sargent-Welch Sci., (Springfield, NJ). The optical brightener standards were obtained from Ciba-Geigy (Greensboro, NC), Verona Chemical Co. (Union, NJ), and Hilton-Davis (Cincinnati, OH).

Sample and Standard Preparation

Samples were prepared by vigorously stirring 2.5 g of detergent in 50 ml of mobile phase then diluting 2 ml into 25 ml for the working solution.

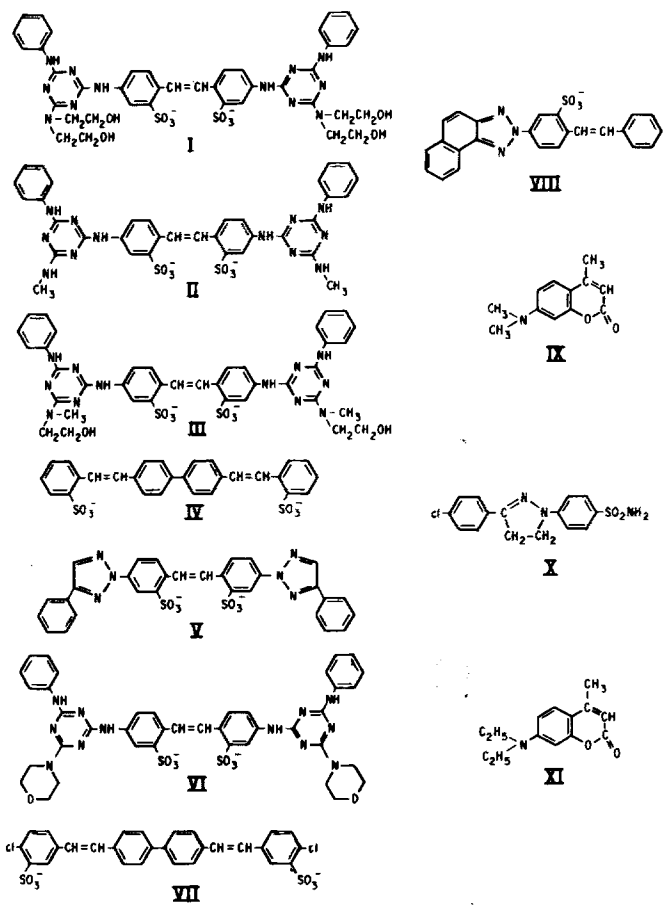

FIG. 1. Optical brighteners studied: I, bis (anilino-dihydroxyethyl-aminotriazinylamino) stilbene disulfonate; II, bis (anilino-methyl-amino-triazinylamino) stilbene disulfonate; III, bis (anilinohydroxy-ethylmethylamino-triazinylamino) stilbene disulfonate; IV, bis (styrylsulfonate) biphenyl; V, bis (phenyl-triazolyl) stilbene disulfonate; VI, bis (anilino-morpholino-triazinylamino) stilbene disulfonate; VII, bis (chlor-sulfostyryl) biphenyl; VIII, naphthotriazolyl stilbene sulfonate; IX, dimethylaminomethyl coumarin; X, (chlorophenyl-pyrazolinyl) benzenesulfonamide; XI, diethylaminomethyl coumarin.

Standards were prepared by weighing 50 mg of brightener into a 100-ml volumetric flask and filling to the mark with mobile phase. The working solution was prepared by diluting a 2-ml aliquot to 100 ml.

HPLC

All mobile phases were filtered through a 5-μm millipore filter before use. Flow rates varied from 1 to 2 ml/min and 20 μl injections were used throughout. Using a C_8 column with acetonitrile/methanol/water (27.5:12.5:60) containing 0.05 M dibasic ammonium phosphate; brighteners I-VII were separated as shown in Figure 2.

All of the straight reverse phase separations to follow resulted in this same elution order, and switching to the Zorbax ODS column yielded a similar chromatogram with slightly longer elution times and small variations in resolution. To chromatograph the remaining 4 brighteners (VIII-XI) the ratio of acetonitrile and methanol to water was raised to 40:10:50 and the buffer remained the same. Figure 3 shows the separation achieved on C_8 and again the elution times and resolution are only slightly different when switching to an ODS column.

In an attempt to have some reversals of elution orders or vast differences in selectivity, paired ion chromatography was used. By simply adding tetraethyl ammonium bromide to the mobile phase which was used in Figure 3, a paired ion was formed with brightener VIII. Since that brightener is the only ionic sulfonate of the 4 it is selectively retained and a reversal of elution order between VIII and IX can be seen in Figure 4. To further enhance this paired ion effect we substituted tetrabutyl for the tetraethyl salt; the resulting chromatogram was identical for brighteners IX-XI, but VIII was retained for 30 min.

A more complex effect of paired ion formation with brighteners I-VI is illustrated in Figure 5. Hexadecyltrimethyl ammonium bromide as the pair reagent on a RP-2 column has greatly effected the chromatography.

The resulting chromatogram shows a reversal in elution order of brighteners V and VI as well as a major switch in the retentions of brighteners II, III and IV. These separations would be very useful as tools to confirm the identity of a questionable brightener found by the reverse phase procedure. If the sample peak matched the standard brightener peak by both ion-pair and reverse phase, its identity is almost unquestionable.

During the comparison of different column characteristics the new radially compressed column concept was also investigated. As Figure 6 illustrates, the brightener separation on these C_{18} cartridges are very similar to those obtained on standard stainless-steel columns, but with the

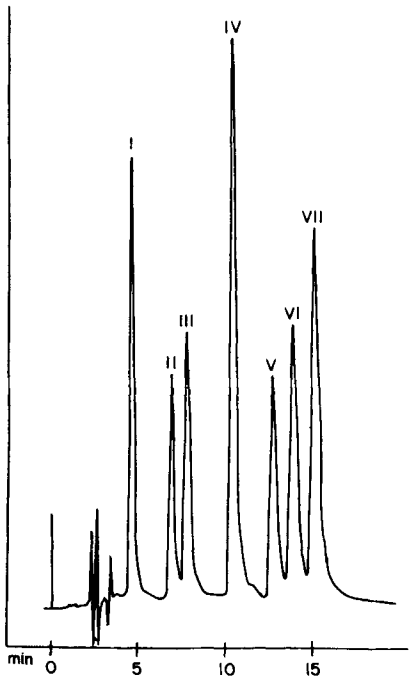

FIG. 2. Chromatogram of optical brighteners I-VII on Zorbax C_8 with 27.5:12.5:60 acetonitrile/methanol/water containing 0.05 M dibasic ammonium phosphate; flow rate 1 ml/min.

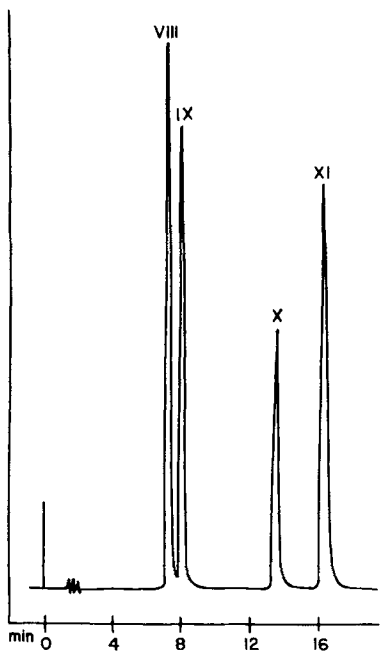

FIG. 3. Chromatogram of brighteners VIII-XI on Zorbax C_8 with 40:10:50 acetonitrile/methanol/water containing 0.05 M dibasic ammonium phosphate; flow rate 1 ml/min.

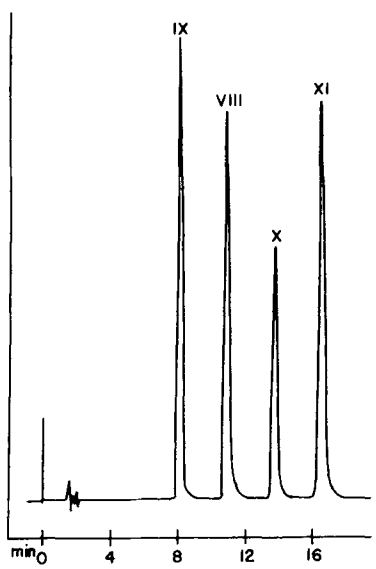

FIG. 4. Chromatogram of brighteners VIII-XI on Zorbax C_8 with 40:10:50 acetonitrile/methanol/water containing 0.01 M tetraethyl ammonium bromide at pH 7.5 with dibasic ammonium phosphate; flow rate 1 ml/min.

same mobile phase as that used in Figure 2, brightener VII elutes under peak VI.

A paired ion separation on a radially compressed C_{18} cartridge is shown in Figure 7. In this case brighteners I-VI are chromatographed with 45:55 acetonitrile/water containing 0.01 M tetrabutyl ammonium hydrogen sulfate at pH 7.5 with dibasic ammonium phosphate. The resulting elution order is the same as that obtained with the paired ion separation shown in Figure 5.

RESULTS AND DISCUSSION

Through the versatility of reverse phase and paired ion chromatography, these 11 brighteners are separated on either of 4 different column types and 5 mobile phases can be used. Depending on the applications, qualitative and

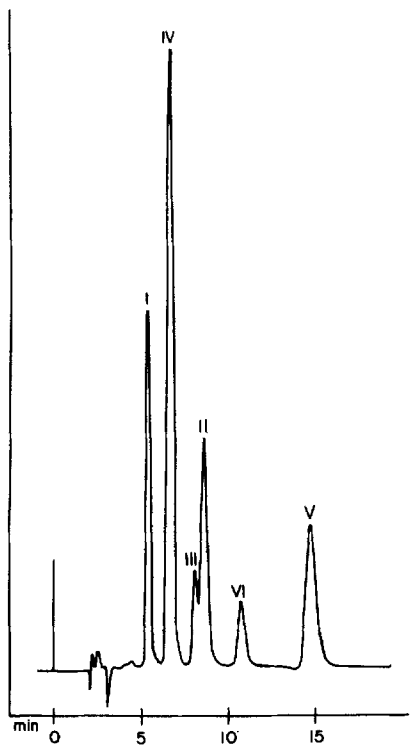

FIG. 5. Chromatogram of brighteners I-VI on LiChrosorb RP-2 with 48:52 acetonitrile/water containing 0.01 M hexadecyltrimethyl ammonium bromide at pH 7.5 with dibasic ammonium phosphate; flow rate 1 ml/min.

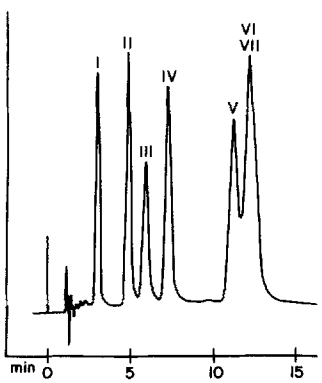

FIG. 6. Chromatogram of brighteners I-VII on a radially compressed C_{18} cartridge with 27.5:12.5:60 acetonitrile/methanol/water containing 0.05 M dibasic ammonium phosphate; flow rate 2 ml/min.

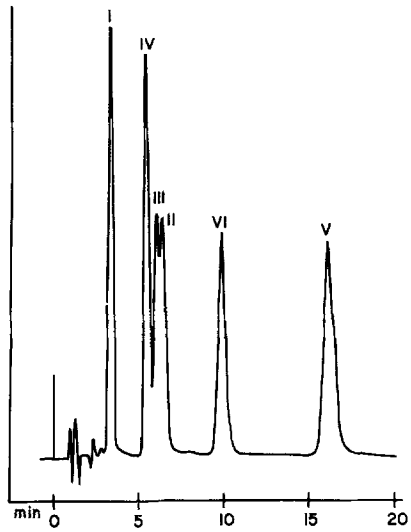

FIG. 7. Chromatogram of brighteners I-VI on a radially compressed C_{18} cartridge with 45:55 acetonitrile/water containing 0.01 M tetrabutyl ammonium hydrogen sulfate at pH 7.5 with dibasic ammonium phosphate; flow rate 2 ml/min.

TABLE I

Brightener Found in Six Separate Analyses of the Same Detergent (%)

	Brightener III	Brightener V
	0.280	0.0860
	0.273	0.0830
	0.280	0.0845
	0.273	0.0830
	0.283	0.0853
	0.278	0.0855
Mean	0.278	0.0846
Standard deviation	0.004	0.0013
Coefficient of variation	1.4%	1.5%

TABLE II

Recovery Study of Three Brighteners in One Formulation

Brightener	Formulation (mg/ml)	Injected (μg)	Recovered (μg)	Recovery (%)
I	0.004	0.040	0.040	100.0
III	0.006	0.060	0.061	101.7
VI	0.012	0.120	0.122	101.7

TABLE III

Comparison of Results Obtained by HPLC and TLC

Product	Brightener	HPLC (%)	TLC (%)
A	III	0.70	0.70
B	III	0.13	0.12
C	III	0.21	0.23
	VIII	0.25	0.22
D	VI	0.09	0.11

TABLE IV

Optical Brighteners in "Off the Shelf" Detergent Products by HPLC (%)

	Brightener						
	I	III	IV	V	VI	VIII	XI
Detergent powders							
A		0.15					
B	0.20						
C		0.11	0.06				
Liquid detergents							
D					0.12	0.05	
E	0.08					0.05	
F		0.06		0.10			
G							0.07
H		0.50				0.06	
I			0.14			0.08	
Bleach boosters							
J					0.10	0.10	
K		0.06					
L					0.05	0.01	
Fabric softener							
M		0.11					

quantitative work is done easily and quickly on all types of detergent products. If the brighteners are known prior to the analysis, simply choose the column and mobile phase with which those brighteners separate and elute the quickest. If they are unknowns, the conditions described in Figures 2 and 3 would be the best place to start in their determination, followed by one of the paired ion separations to back up the identifications if necessary.

The dependability of the quantitative nature of these methods has been tested through several precision and accuracy determinations. Tables I and II illustrate 2 studies performed on known, exactly prepared formulations. Calculations were based on peak heights *vs* weights of samples and standards injected.

A comparison between the results using these procedures and those obtained by an adaptation of the Schulze (1) TLC procedure shows close agreement between samples. Table III lists results obtained by both methods on several "off the shelf" products. Brighteners III, VI, and VIII are by far the most commonly found in products ranging from powdered and liquid detergents to fabric softeners, presoaks and bleach boosters. The sample chromatograms are identical to those of the standards since no interfering components have been detected under these conditions. As Table IV shows, a random sampling of these products can contain single brighteners or mixtures of just about any type and level. Since their particular stabilities, fabric substantivity, costs and fluorescence activity dictate where they are used and in what amounts, there is no way to predict which will be present and at what level. The use of one or more of these HPLC methods makes the determinations fast and accurate.

REFERENCES

1. Schulze, J., T. Polcaro and P. Stensby. Soap Cosmet. Chem. Spec. 50:46 (1974).
2. Kirkpatrick, D., J. Chromatogr. 121:153 (1976).
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