Application of Spectrophotometric Methods to the Determination of Glycerine Color

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UP to the present time the measurement of glycerine color has been accomplished by visual means. The color standards have ranged from the descriptive type, such as "very light" and "straw color" to comparison with the Lovibond glass slides. Visual comparisons have been set up for C.P. and U.S.P. grades using the standard colorimetric solutions (N.F. and U.S.P.) to define color limits. The glass slides used in the Lovibond tintometer are applicable to the measurement of the color of High Gravity or Dynamite grades in terms of an arbitrary scale.

Lovibond determinations have the inherent disadvantages of visual methods, such as eye fatigue, individual differences, limited objectivity of approach, and color vision defects. Furthermore, at the present time the apparatus used and parts thereof are not easy to obtain (1).

Since spectrophotometers have become a part of the standard equipment in many laboratories, we decided to study the application of this instrument to the problem of glycerine color measurement.* Because glycerine color is commonly reported in Lovibond units, one of the objects of our work was to develop a spectrophotometric method for determining color in terms of these units. It seemed probable that under the proper conditions this could be accomplished with greater accuracy and reliability than is obtained by the use of Lovibond glasses. That this can be achieved is strongly indicated by the results obtained in the present study. We feel confident that, with further refinement through cooperative investigation, the spectrophotometric method can be a useful addition to currently accepted methods for the determination of color in glycerine.

Experimental

The apparatus used by our laboratory in this work consisted of a Wesson type colorimeter and set of Lovibond glass slides, and a Coleman Universal spectrophotometer (Model 11) with 13-mm. square cuvettes. The cooperating laboratories used comparison colorimeters with Lovibond glasses, four Beckman spectrophotometers (Model DU), and one Coleman Junior spectrophotometer. Fifty-five glycerine samples were used in the development of the proposed method, and 10 additional samples were used in verification.

In the beginning of this study eight samples of high-gravity glycerine were measured spectrophotometrically over the wave length range 370 to 720 mμ, in order to cover the whole visible range. Figure 1 shows the curves obtained when optical density was plotted against wave length. Lovibond color values also were determined for these samples, in the usual way. Several statistical methods were applied to these data to determine the best wave lengths to be used when converting optical density data to Lovibond values. One of these methods was the calculation of correlation coefficients between the two sets of measurements. Another involved the determination of the mean deviation from the average ratios between Lovibond color and optical density at vari-

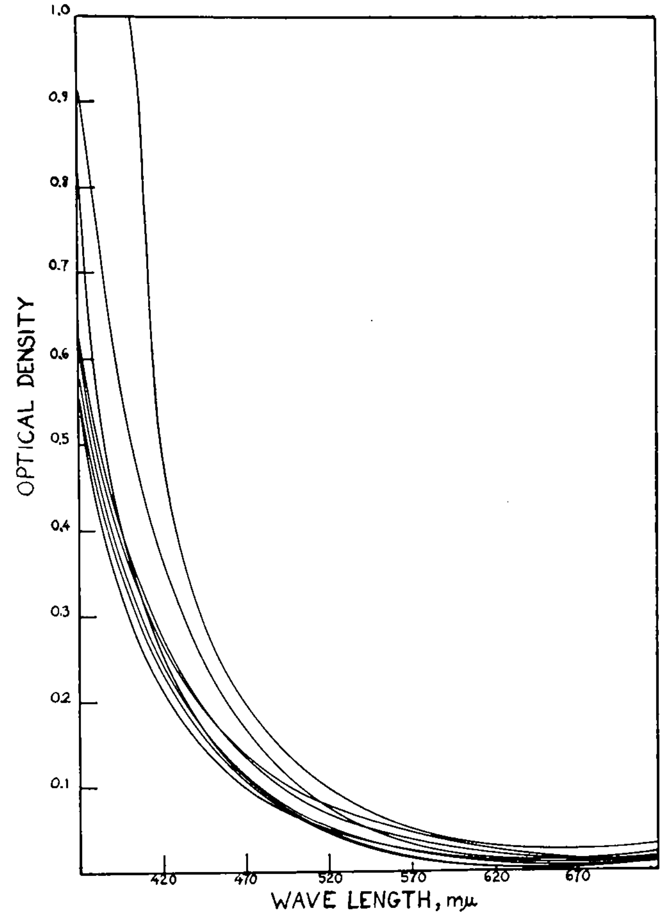

FIG. 1. Optical density vs. wave length for eight high-gravity glycerine samples. Coleman Model 11 spectrophotometer, using 13-mm. cuvettes.

TABLE I

Results of Statistical Analysis of Lovibond and Optical Density Data on Eight Glycerine Samples

Wave Length Milli-microns	Correlation Coefficients Between		Per Cent Mean Deviation from Average Ratios	
	Lovibond Red and Optical Density	Lovibond Yellow and Optical Density	Lovibond Red/ Optical Density	Lovibond Yellow/ Optical Density
420	......	0.72	13	12
440	0.73	.82	11	12
460	.78	.84	12	14
480	.90	.78	8.3	17
500	.94	.73	7.4	18
520	.96	.67	9.0	19
540	.95	......	14	27
560	.94	......	17	30

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* The use of photo-cell instruments for determination of oil and tallow colors has been the subject of considerable study (1, 2, 3, 4).

TABLE II

Comparison of Visual and Spectrophotometric Methods of Determining Lovibond Color of Glycerine

Sample	Visual Observed Lovibond Yellow Color																		Spectrophotometric Graphical† Yellow Color from Optical Density at 440 mμ								
	Laboratory: A					B		C			D	ML			Mean Value*	Max. Deviation	Mean Deviation	A	B	C	D		ML	Mean Val.*	Max. Deviation	Mean Deviation
	Five Observers					Two		Three			One	Three						Beckman	Beckman	Beckman	Beckman	Coleman Jr.	Coleman No. 11			
1	5	5	5	7	6	7	6	5	5	6	5	6.5	5.5	5.5	5.7	1.3	0.64	4	6	5	6	5.5	4.5	5.1	1.1	0.67
2	9	10	10	9	10	13	11	9	9	12	10	10.5	9.5	9.0	10	3.0	0.86	10	12	11	12	12	9.5	11	1.5	0.92
3	15	15	15	14	15	35	20	17	17	23	15	16	15	15	16	19	2.9	16	18	17	17	18	15	17	2	0.83
4	21	19	15	19	19	35	23	19	20	20	17	22	20	22	20	15	2.5	20	23	20	22	22	19	21	2	1.3
5	31	19	16	19	19	35	32	21	20	20	21	23	20	23	23	12	4.4	21	25	23	24	25	21	23	2	1.5
6	31	19	20	20	17	35	31	22	19	25	20	22	22	22	23	12	4.0	21	24	23	22	22	20	22	2	1.0
7	32	20	19	23	20	35	30	26	23	25	25	27	21	27	25	10	3.6	24	27	25	24	25	22	24	3	1.2
8	34	21	20	25	26	70	30	29	26	25	27	30	23	....	26	44	6.2	25	28	27	28	28	25	27	2	1.2
9	35	29	30	29	35	70	42	38	39	35	30	35	33	....	34	36	5.8	33	36	33	35	36	32	34	2	1.5
10	55	40	38	35	40	70	51	50	50	50	50	50	50	....	48	22	6.4	51	57	52	55	53	49	53	4	2.2
															Overall Average Deviation	3.7								Overall Average Deviation	1.2	

†Values determined from optical density data by means of the graphs, Figures 2 and 3.

*In computing the mean values, any single value whose deviation from the mean of the other values was greater than five times the average deviation of the others was discarded.

TABLE III

Comparison of Visual and Spectrophotometric Methods of Determining Lovibond Color of Glycerine

Sample	Visual Observed Lovibond Red Color																		Spectrophotometric Graphical† Red Color from Optical Density at 520 mμ								
	Laboratory: A					B		C			D	ML			Mean Value*	Max. Deviation	Mean Deviation	A	B	C	D		ML	Mean Val.*	Max. Deviation	Mean Deviation
	Five Observers					Two		Three			One	Three						Beckman	Beckman	Beckman	Beckman	Coleman Jr.	Coleman No. 11			
1	1.5	1.6	1.3	1.5	1.3	2.2	1.7	1.8	1.4	1.6	1.8	1.0	1.2	1.5	1.5	0.7	0.21	1.5	1.9	1.6	2.0	1.8	1.3	1.7	0.4	0.22
2	2.2	2.2	1.9	2.0	1.9	3.0	2.5	2.2	1.8	1.9	2.5	1.5	1.5	2.0	2.1	0.9	0.31	2.0	2.3	2.2	2.7	2.6	1.4	2.2	0.8	0.33
3	3.9	3.6	3.4	3.6	3.5	3.7	3.8	3.6	3.6	3.5	3.6	3.0	3.5	3.2	3.5	0.5	0.16	3.8	4.1	4.2	4.2	4.4	3.0	4.1	1.1	0.32
4	4.3	4.2	4.0	4.1	4.1	4.4	4.1	4.5	4.2	4.2	4.2	4.5	3.8	3.7	4.1	0.6	0.19	4.3	5.0	4.5	4.7	4.8	3.4	4.7	1.3	0.38
5	4.1	4.1	3.5	3.9	4.0	4.7	4.7	4.0	4.0	3.8	4.2	4.0	4.3	4.0	4.1	0.6	0.23	4.3	5.1	4.2	4.6	5.1	3.9	4.5	0.6	0.40
6	4.3	4.2	4.0	4.0	4.1	4.6	4.7	4.2	4.3	4.2	4.5	3.3	3.5	3.5	4.1	0.8	0.31	4.3	4.9	4.5	4.7	4.8	3.5	4.6	1.1	0.35
7	4.8	4.6	4.3	4.6	4.5	5.0	5.0	4.9	5.1	4.8	4.9	3.5	4.5	4.0	4.6	1.1	0.32	4.7	5.4	5.3	5.1	5.2	4.1	5.0	0.9	0.37
8	5.2	4.9	4.6	4.8	4.7	5.7	5.1	5.1	5.0	4.5	5.3	5.0	5.2	....	5.0	0.7	0.24	5.2	5.7	5.8	5.9	5.7	4.5	5.7	1.2	0.33
9	6.9	6.3	6.3	6.1	6.3	9.0	8.0	7.3	7.8	7.2	7.3	6.5	7.0	....	7.1	1.9	0.64	7.2	7.9	7.5	7.5	7.6	6.2	7.5	1.3	0.35
10	10.6	9.9	10.0	10.0	9.5	12.0	12.0	10.8	10.4	10.3	10.6	8.0	9.0	....	10.2	2.2	0.78	10.5	11.6	10.5	10.6	10.8	9.0	10.8	1.8	0.57
															Overall Average Deviation	0.34								Overall Average Deviation	0.36	

†Values determined from optical density data by means of the graphs, Figures 2 and 3.

*In computing the mean values, any single value whose deviation from the mean of the other values was greater than five times the average deviation of the others was discarded.

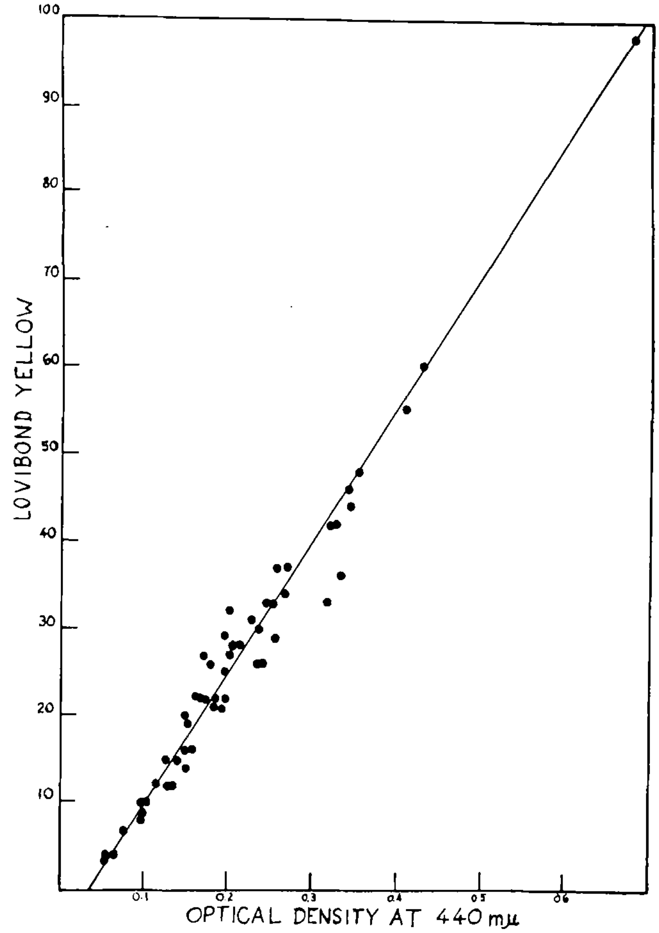

FIG. 2. Relationship between optical density at 440 mμ and Lovibond yellow color, 13-mm. cuvettes.

ous wave lengths. Results from these two methods are listed in Table I.

From Table I it is seen that the wave lengths giving the highest correlations between optical density values and Lovibond red and yellow colors are about 530 mμ and 450 mμ and those showing minimum ratio deviations are about 490 mμ and 430 mμ, respectively. Since it is obvious from the data that the wave length is not highly critical, at least over a range of about 30 mμ, a tentative selection of 520 mμ for red and 440 mμ for yellow was made. The validity of these selections was confirmed by the good correlation obtained in subsequent work with large numbers of glycerine samples.

In the next phase of the work each cooperating laboratory obtained spectrophotometric and Lovibond data on 8-10 samples of glycerine. Measurements on these samples, of which there were 47 in all, were also made by the authors. The total data from 55 samples were used to calculate the relationships between optical density values made at 440 mμ and 520 mμ and Lovibond yellow and red colors, respectively. Two linear equations were found by the method of least squares. They are:

for yellow: $Ly = 153D_1 - 5.7$
for red: $Lr = 80.7D_2 - 0.55$

where

D_1 = optical density at 440 mμ for 13 mm. cell
D_2 = optical density at 520 mμ for 13 mm. cell
Ly = Lovibond yellow color
Lr = Lovibond red color

The degree of conformity between the data and the equations is shown by Figures 2 and 3. It will be noted that the curves show a positive optical density value at zero Lovibond. This presumably represents the average light transmission loss due to the several air-glass interfaces of the Lovibond glass combinations. Since it is usually necessary to use several Lovibond glasses to match a given glycerine sample, a significant part of the color intensity of the sample is "matched" by the light loss at the air-glass interfaces. Spectrophotometric measurements involve no net loss of this kind so it is to be expected that zero optical density will not be reached on extrapolation of the line to zero Lovibond.

For verification of this method of conversion, a set of 10 glycerine samples covering a representative color range was prepared. Spectrophotometric and Lovibond data were obtained for each sample by our laboratories and by the cooperating laboratories. The data obtained are listed in Tables II and III. They indicate that satisfactory agreement can be expected between different laboratories using visual and spectrophotometric methods to obtain Lovibond color and that values obtained spectrophotometrically are at least as reliable as values obtained visually. It should

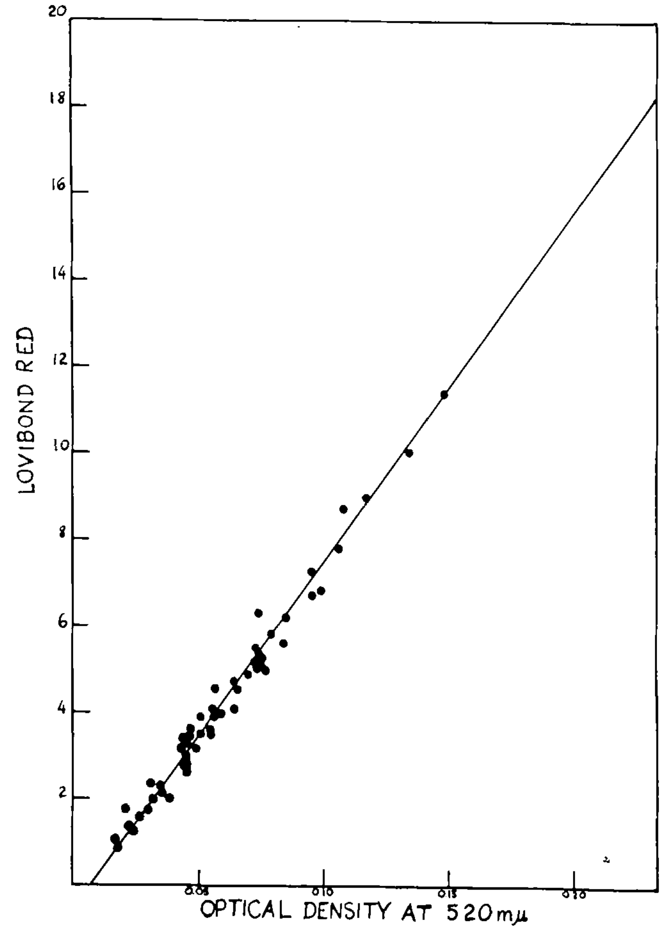

FIG. 3. Relationship between optical density at 520 mμ and Lovibond red color, 13-mm. cuvettes.

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[1] Presented at 22nd annual fall meeting, American Oil Chemists' Society, New York City, Nov. 15-17, 1948.

be clearly understood that the methods described are purely preliminary and have no official status.

Summary

A method has been developed by which spectrophotometrically measured glycerine color can be expressed in terms of Lovibond units. The yellow and red color values are determined, by means of two statistically derived linear relationships, from optical density measurements at 440 mμ and 520 mμ, respectively. The conversion from spectrophotometric data to Lovibond color units may be done graphically and the results are at least as reliable as the results of repeated visual measurements.

Acknowledgment

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The Effect of a Non-ionic Detergent on the Detergency of Alkylaryl Sulfonates and Soap in Hard Water*

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Introduction

IT has been recognized for many centuries that soap has certain deficiencies as a detergent in hard water. During the past two or three decades much research has been devoted with considerable success to the development of detergents which overcome the less desirable properties of soap in hard water. Among these latter products of promise are the non-ionic detergents. One purpose of this paper is to show the effect of one of these non-ionic detergents on the detergency of soap. It has likewise been known for several years that the alkylaryl sulfonate type of detergent, although excellent for many applications, is deficient in detergency for the washing of cottons. In spite of this deficiency the alkylaryl sulfonates foam profusely whereas the non-ionics are generally not good foam producers. Consequently a second purpose of this paper is the determination of the effect of a non-ionic on the detergency of alkylaryl sulfonates in the washing of cotton.

The employment of synthetic detergents with soap has not received great attention. McDonald (1) described some experimental work on a salt water soap which contained admixtures of soap with synthetic detergents, including some non-ionics. Recently, Barker (2) reported some preliminary results on the effect of certain non-ionic detergents on the detergency of the alkylaryl sulfonates. The purpose of this paper is to present new data on the effect of a non-ionic detergent, Renex,[1] a polyoxyalkylene derivative of mixed fatty and resin acids, on the detergency of the two major groups of anionic detergents, soap and alkylaryl sulfonates, as measured in the laboratory.

In view of the predominant importance in both commercial and home laundering of cotton washing, the evaluation of detergent systems has been devoted principally to this fabric. There are many methods of measuring detergency in the laboratory, but most of them consist of removing from a fabric a synthetic soil composed of carbon and some form of oil or grease by washing in a laboratory machine. The present study was conducted by washing a synthetically soiled cotton muslin with a detergent solution in a Launder-O-Meter type machine. The detergency is measured by determining the light reflectance of the soiled fabric before and after washing. The detergent efficiency is calculated by the following formula:

$$\text{Detergent efficiency} = \frac{R_w - R_s}{R_o - R_s} \times 100.$$

Where R_w = Reflectance of the washed fabric
R_s = Reflectance of the soiled fabric
R_o = Reflectance of the unsoiled, unwashed fabric.

In this discussion Relative Detergent Efficiency is the ratio of the efficiency of one detergent system relative to the efficiency of any other detergent system taken arbitrarily as 100.

EXPERIMENTAL

Preparation of Standard Soiled Fabric

One of the most influential factors in detergent testing is the character and method of preparation of the soiled fabric. The standard soiled fabric used in this study is essentially that of Vaughn and Smith (3). The principal differences are dictated by the smaller scale of operations.

In this work strips, 10 in. x 120 in., of a standard muslin are immersed in a 0.1 N sodium hydroxide solution and maintained in it for two minutes. The strips of fabric are then rinsed three times in distilled water at 80°C. for five minutes each time. The fabric is then placed in a solution of 15 g. of sodium stearate and 3,300 ml. of distilled water (at 80°C.) and are thus washed at that temperature by gentle stirring for two minutes. After having been washed, the fabric is rinsed three times at 80°C. and three times at room temperature in distilled water for five minutes each time. The clean fabric is squeezed through the rolls of a washing machine wringer and ironed immediately. Care is taken during these operations to maintain the cloth submerged below the surface of the solutions, and the solutions are stirred frequently to obtain thorough washing and rinsing.

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* Presented at the 22nd fall meeting, American Oil Chemists' Society, New York City, Nov. 15-17, 1948.

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