The Photometric Determination of the Color of Certain Glyceride Oils*

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A METHOD is presented for the photometric evaluation and interpretation of the visual color of tallows and greases. Various aspects involved in the proper measurement of color are discussed. Comprehensive systems for the photometric color-grading of these oils based upon absorption data derived by this method have been devised and are furnished.

The fundamentals of this method should be applicable to other oils outside the scope of this paper. Considering that one of the most salient shortcomings with regard to visual methods for the evaluation of color lies in the very fact that they are visual, it would appear highly desirable to possess some means of determining the color of oils in which this personal factor is entirely eliminated. The results procured by such a method would not be inherently subject to the numerous variations in individual conceptions of color. Ocular fatigue would be obviated, and, it would be rendered possible for a dichromat or color-blind person to determine the color of an oil. Incidentally, an interesting paper concerning the Lovibond system has been published by Gibson and Harris (1).

Also, in visual methods difficulties involving accuracy and precision are frequently encountered when recourse to a trichromatic combination is made in an attempt to match closely the color of an abnormal oil. However, as will be seen, a trichromatic measurement is essential to the proper measurement of color. The normal physiological sensation of color is based upon the effect of a trichromatic stimulus upon the retina of the eye, involving the relative intensities of the primary hues, red, green, and blue. It is essential that a satisfactory method for color evaluation be characterized by a means of determining the color value, hue, and saturation, and, this is achieved only through a measurement of the three previously mentioned chromatic stimuli.

The photometric method to be described meets all the suggested requirements, since it provides:

1. Elimination of the personal factor in chromatic measurements.
2. A continuous scale measurement of color value (brilliance).
3. A method of determining chromatic functions.
4. A means of interpreting visual color from photometric data.

Apparatus

A photo-electric photometer (Fisher) equipped with the following three filters was utilized in this investigation:

1. Corning Noc. 2403 + 9780 (½ Std. T.).
2. Corning No. 4010.
3. Corning No. 5543.

For the purpose of brevity the above mentioned filters from this point on will be referred to as R, G, and B respectively.

Precision absorption cells having optical depths of 2.5, 10.0, 20.0, and 50.0 mms., or 3.0, 8.0, 20.0, and 50.0 mms. are suggested for usage.

Procedure

A clear sample of the oil is first prepared, using an inert filter aid, and anhydrous sodium sulphate, if necessary. Maintain the sample in a liquid state, and at a temperature of 45-50° C. Then employing successively in the photometer the filters R, G, and B, determine the optical densities of the sample, against a blank of distilled water, in the three spectral regions so isolated, using absorption cells of appropriate optical depth so as to yield values from 0.10-0.70.

In the case of extremely dark oils, where the absorption is too high for the small cell, it is usually satisfactory to obtain data from carefully prepared dilutions, say 1:1 or 1:3 with some non-interfering solvent of low volatility, such as, a high-grade light mineral oil. Convert all optical densities obtained to the standard basis of a 1.0 cm. cell. Record the (G) filter optical density as the color index (degree of darkness). Calculate the B/G and G/R absorption ratios, and from them determine the composite Hue, the Hue Indices, and Saturation Indices as follows:

Hue

$$\text{B/G} \begin{cases} <2.45 = \text{Blue} \\ >2.95 = \text{Yellow} \end{cases}$$

$$\text{G/R} \begin{cases} >2.45 = \text{Green} \\ <2.95 = \text{Red} \end{cases}$$

NOTE: Hue ratios of 2.45 to 2.95 are considered the criteria of a normal oil. In samples where the hue ratio lies within these limits, it is not necessary to record the hue nor calculate the following hue index, except when the specific system of grading is employed.

Hue Index

$$\text{Blue} = \frac{2.7}{\text{B/G}} \qquad \text{Yellow} = \frac{\text{B/G}}{2.7}$$

$$\text{Green} = \frac{2.7}{\text{G/R}} \qquad \text{Red} = \frac{\text{G/R}}{2.7}$$

NOTE: Values of 1.0 for both hue indices, of course, would indicate an oil of standard hue.

Saturation Index

$$\text{Saturation Index} = (\text{Hue Index} - 1.0)\ \text{G}$$

NOTE: Saturation indices of 0.0 would indicate an oil of standard saturation.

Experimentation

Photometric data were obtained on a large number of samples of tallow and grease according to the previously described procedure. Lovibond color readings were determined for interest, and normal visual conceptions of the hues of the samples in the solid state were noted. Some of the resultant data covering representative samples of oils of various color types are recorded in Table I.

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TABLE I.

Sample No.	Opt. Dens. (Cell 1.0 cm.) Filters B	G	R	Opt. Dens. Ratios B/G G/R	Lovibond Color Cell 1"	Visual Hue
1	0.580	0.200	0.080	2.90 2.50	35/3.2	Gray
2	0.473	0.173	0.062	2.73 2.79	23/2.6	Sl. Fawn-Gray
3	0.455	0.157	0.064	2.90 2.48	23/2.5	Gray
4	1.236	0.446	0.164	2.77 2.72	70/7.2	Brown-Gray
5	0.650	0.245	0.150	2.65 1.63	50/3.4	Sl. Green
6	2.625	1.000	1.775	2.63 0.56	Not Readable	V. Green
7	3.450	0.900	1.000	3.83 0.90	Not Readable	Sl. Yellow-V. Green
8	1.710	0.390	0.315	4.38 1.24	85/3.6	Yellow-Green
9	1.718	0.409	0.291	4.20 1.41	72/4.4	Yellow-Green
10	3.150	0.6875	0.600	4.58 1.15	155/6.6	Yellow-Green
11	2.985	0.560	0.420	5.33 1.33	120/5.6	Yellow-Green
12	0.850	0.286	0.072	2.97 3.97	38/5.9	Sl. Red

It was observed that light colored samples, lying in that region where color perception is acute, were characterized by a hue described as a very slight fawn-gray. They possessed B/G and G/R optical density ratios of 2.7 $\pm$ 0.25 approximately, and Lovibond color ratios of closely 10.0 yellow to 1.0 red. These two chromatic ratios were thereupon arbitrarily selected as the criteria of an oil possessing a standard or neutral hue. Concomitant changes in hue are manifested by variations in these optical density ratios. The effects of these ratio deviations from the normal are shown diagramatically in Figure 1. This diagram shows the effect of the chromatic ratios B/G and G/R upon the resultant visual hue of an oil. In the center of the hue-rectangle, connected by a vertical line, are the standard B/G and G/R ratios denoting an oil of standard composite hue. As the B/G ratio increases or decreases the hue of the oil becomes yellower or bluer respectively; similarly, as the G/R ratio increases or decreases the oil becomes redder or greener respectively. In each of the foregoing cases it will be noted that one chromatic ratio remains fixed (Standard).

If both chromatic ratios vary from the standard, the resultant composite hue will be dependent upon the direction and amounts (given by the Hue Indices) of these variations from the standard. For example, if the B/G and G/R ratios are high but equal, the oil would possess an orange hue, similarly if these ratios are low but equal, the oil would possess a blue-green hue. This is represented by the vertical lines at the sides of the rectangle. The effects of combinations of high B/G and low G/R ratios, and vice versa, are indicated by the diagonal lines in the diagram. For instance, an oil exhibiting a correspondingly high B/G and low G/R ratio (equal hue indices) would possess a yellow-green hue. It follows that there would exist an indeterminate number of composite hues, but the predominating hue would always be the one possessing the higher Hue Index. It would be pertinent at this point to mention that although the hue schematic diagram for the purpose of clarity was made comprehensive, actually none of the numerous oil samples examined showed B/G ratios under 2.45. It is evident from this that a blue hue displayed individually or as a composite is not to be expected, at least, in the case of tallows and greases.

Development

Several systems of photometric color grading as applied to tallows and greases have been devised, based upon the foregoing method. The first, a specific system, involves the direct use of: the color index as the expression of the degree of darkness; the hue index as the measure of the hue deviation from standard or neutral; and the saturation index as the measure of the visual intensity of the hue.

The second system is a graduated one, the degree of darkness being expressed through a simple series of photometric numbers correlated with a graduated scale of color index. At certain prescribed points in the color index scale successive increases in the magnitude of the gradations are involved, that is, the photometric grade tolerance is more liberal with respect to the darker oils. In this system the visual

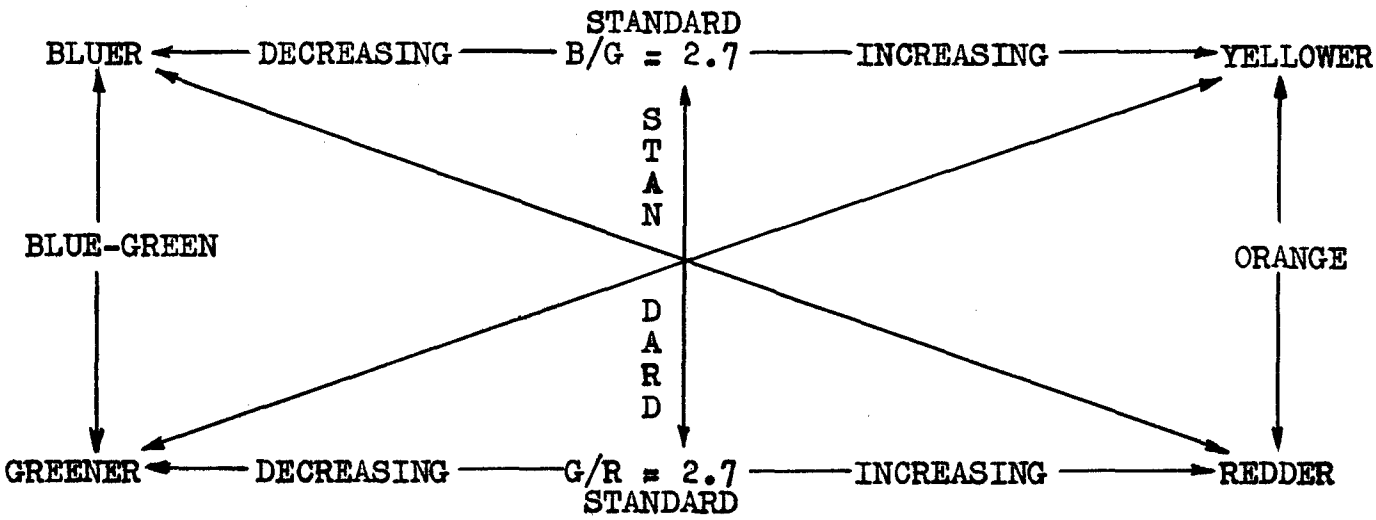

FIGURE 1. Showing the effect of higher and lower chromatic ratios upon the resultant hues of an oil.

character of an off-standard hue is expressed in simple descriptive terms, namely, slight, medium, and very, through interpretation from the hue index. In defining the color of an oil, note that the chromatic ratios B/G and G/R determine the character of the two necessary individual hues. Each ratio is calculated, as previously described, to yield a value termed the Hue Index which is a mathematical convenience enabling a simple direct comparison of the amount each hue varies from the standard. The relationship between the two individual hues as indicated by their respective hue indices, of course, determines the composite hue. The method of interpreting photometric data for application to this system is illustrated in Table II.

TABLE II.

Shows the Application of Photometric Data to Color Grading System No. 2.

Color Density Index G-Filter 1.0 cm. Cell	Photometric Grade No.	Color Density Index G-Filter 1.0 cm. Cell	Photometric Grade No.
0.032	1	0.496	19
0.048	2	0.560	20
0.064	3	0.624	21
0.080	4	0.688	22
0.096	5	0.816	23
0.112	6	0.944	24
0.128	7	1.072	25
0.144	8	1.200	26
0.160	9	1.328	27
0.176	10	1.584	28
0.192	11	1.840	29
0.208	12	2.096	30
0.240	13	2.352	31
0.272	14	2.608	32
0.304	15	2.864	33
0.336	16	3.120	34
0.368	17	3.376	35
0.432	18	3.632	36

Hue (Derived from Ratios B/G and G/R)	Hue Index (Devn. from Std.)		Visual Devn. of Hue from Std.
.....	1.0	=	Standard
.....	1.0 to 1.1	=	Normal
.....	1.1 to 1.7	=	Slight
.....	1.7 to 2.7	=	Medium
.....	> 2.7	=	Very

Alternatively, a photometric number series corresponding to a rising optical density scale of equal gradations, could be set up.

Examples illustrating the mode of tabulating sample data derived by this method, according to the first and second systems of color grading just described, are given in Table III.

Notes

Some deviation from Beer's Law was observed, especially in the case of B and G filter density values involving abnormally green oils. It is possible that the use of suitable interference-type filters or special filter combinations would minimize or eliminate these deviations.

It should be observed that the chromatic functions quoted herein are directly dependent upon optical densities determined within the specific spectral bands isolated by the designated optical filters and, as such, cannot be arbitrarily adopted.

The fact that the two absorption ratios, B/G and G/R, signifying an oil of standard hue, are identical (2.7) is obviously coincidental.

Most of the color variations from the normal in tallows and greases are apparently attributable to the relative amounts present of the chromaphoric compounds, carotin, xanthophyll, chlorophyll-A, and chlorophyll-B. These latter two compounds exhibit,

TABLE III.

Showing the Mode of Tabulating Sample Data According to Color Grading Systems Nos. 1 and 2.

SYSTEM NO. 1

Sample	Color Index	Ratios B/G G/R	Hue	Hue Index	Satn. Index
A	0.500	2.7 2.9	..... Red	1.0 1.07	0.0 0.035
B	0.500	2.7 0.9	..... Green	1.0 3.0	0.0 1.0
C	0.500	4.05 1.35	Yellow Green	1.5 2.0	0.25 0.50
D	0.05	4.05 1.35	Yellow Green	1.5 2.0	0.025 0.05
E	0.086	2.51 1.34	Blue Green	1.08 2.02	0.007 0.088

SYSTEM NO. 2

Sample	Photom. No.	Hue and Devn. From Std.
A	20	....
B	20	..... Very Green
C	20	Sl. Yellow Med. Green
D	3	Sl. Yellow Med. Green
E	5	..... Med. Green

in addition to strong absorption bands in the short-wave region of the visible spectrum, two pronounced but narrow bands at approximately 670 and 640 mμ, respectively. In order to increase the response of the instrument in this latter region of the spectrum the absorption was increased by the use of the monochromatic filter combination (R), as designated under "Apparatus."

Color indices, measurements of the degree of darkness of oils, are expressed as optical density values, basis a 1.0 cm. cell, obtained by using the G-Filter, and, as such, are directly proportional. The fundamentals of this method of color evaluation could, of course, be employed with various types of photoelectric instruments, but actual numerical concordance in inter-laboratory data would be dependent upon the use of standard equipment under prescribed conditions.

Conclusion

A photometric method has been presented for the determination of the colors of tallows and greases.

The relation existing between certain spectral absorption data and the normal visual conception of color has been shown.

The method is both comprehensive and flexible and entirely eliminates the personal factor as involved in a visual method of color-grading, with its attendant disadvantages, variations in individual chromatic conception, ocular fatigue, and the inability of the dichromat to evaluate color.

The method inherently permits the devisal of color measuring systems of a continuous and comprehensive character.

Several systems of color evaluation for tallows and greases adapted to photometric data derived by the foregoing method have been furnished.

It is desired to draw attention to the fact that this technical paper does not possess any official status but is presented by the author with the thought that

it offers some original concepts which might provide another and simple approach to the problem involving the color evaluation of oils by means of photoelectric photometry. Indubitably, considerable further investigation, particularly of a cooperative nature, remains to be performed before a final and universally acceptable photometric method is evolved.

REFERENCES

1. Gibson, K. S., and Harris, F. K., The Lovibond Color System, B. of S. Paper No. 547, Vol. 22, 1927.

Thermal Properties of Fats and Oils

VI. Heat Capacity, Heats of Fusion and Transition, and Entropy of Trilaurin, Trimyristin, Tripalmitin, and Tristearin

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IN previous papers (1) of this series heat capacity data from 180° to 363° K. on cottonseed oil, hydrogenated cottonseed oil, and a cottonseed oil-solvent mixture were reported. The present report presents thermal data between 90° and 373° K. for the simple triglycerides of four commonly occurring fatty acids. The entropy of each compound has been calculated and is reported.

In conformity with the nomenclature recommended by Lutton (2), the three polymorphic forms of the triglycerides are hereinafter referred to as β, β', and α in decreasing order of their melting points. These forms were designated as I, II, and III, respectively, in a previous publication (3) from this laboratory.

Preparation of Samples. The triglycerides were prepared from glycerol and fatty acids according to the method described previously (3). The melting points of the β-form, in Table II, compare favorably with those reported by previous workers (2, 4).

The impurities in trilaurin and tristearin were estimated from measurements of the temperature as a function of the fractions melted. It has been estimated that the purity of the compounds used in this investigation was in each case between 98 and 99 mole per cent. These estimations were made on the assumption of the absence of solid solutions and until means for verifying this assumption are available the thermal values should be considered as minimal values. Since trimyristin and tripalmitin yielded melting point curves as sharp as those of the other two compounds, they were considered to be of the same order of purity.

In each case the material was obtained in the β-form by tempering the solidified sample, contained in the calorimeter, at a temperature slightly (1° to 2°) below the melting point of this form. It was not possible to obtain the relatively fleeting (2) β'-form in the calorimeter which was used in this investigation. Previous work (2, 3) has shown that the α-form of the triglycerides results by rapid or moderately rapidly cooling of the melt. This form was obtained by immersing the calorimeter filled with the melted fat in liquid nitrogen. The thermal examination of the α-forms of trimyristin, tripalmitin, and tristearin was completed without difficulty, since these were sufficiently stable at room temperature for this purpose. However, the heat capacity data on the α-form of trilaurin invariably indicated partial transformation of the sample during the period required for setting up and evacuating the calorimeter, even when the temperature was not allowed to rise above 0° C. Therefore, data for the pure α-form of trilaurin could not be obtained.

Apparatus and Procedure. A detailed description of the apparatus and method was given in the first paper of this series (5). Briefly it is as follows: The samples were sealed in a copper calorimeter which was enclosed in a semi-adiabatic calorimetric system. A measured amount of energy from storage batteries was supplied to the calorimeter. All temperature measurements were made with a single-junction thermocouple. The electrical and temperature measurements were made with a White double potentiometer in conjunction with a high-sensitivity galvanometer. The accuracy of the results is believed to be better than one per cent. Results are reported in terms of the defined calorie, *i.e.*, 1 cal. = 4.1833 int. joules. All weights were corrected to vacuum.

Results and Discussion

Heat Capacity. The results of the heat capacity measurements made on the α- and β-forms of trimyristin, tripalmitin, and tristearin, and the β-form of trilaurin are presented in Table I.

Measurements were not made below 192° K. on the triglycerides in the α-form.

It should be noted that in all of these triglycerides apparent melting is evident at temperatures considerably below the final melting points. This phenomenon is strikingly illustrated by the change in slope of the curve reproduced in Figure 1 in which the heat capacity is plotted as a function of temperature.

The possibility was considered that this change in the rate of increase of the specific heat might result from a change in the crystal structure (polymorphic change), *i.e.*, it might represent a true change in specific heat of the compound. However, the calorimetric data strongly indicates that some melting actually occurs at these low temperatures, and this interpretation is further substantiated by dilatometric measurements previously reported for these triglycerides (6), in which premelting of the samples

[1] The experimental work reported herein was carried out in part by one of the authors and in part by G. D. Oliver under the direction of A. E. Bailey while the latter were employed with this laboratory.

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