Comparison of Visual and Automated Colorimeter for Refined and Bleached Cottonseed Oils

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ABSTRACT: Color as a fundamental quality of edible oils has been determined primarily by visual comparison. The automatic colorimeters introduced recently made it possible to avoid operator variability associated with visual color measurement. The feasibility of using an automatic colorimeter, Colourscan, to measure the color of refined and bleached cottonseed oils was investigated. Good agreement, $r^2 = 0.99$, between automatic color readings vs. visual color measurement by using the Lovibond–AOCS Color Scale was obtained. Near-linear correlation of light paths from 133.4 to 2.5 mm permits dark oil to be assessed with the automatic colorimeter.

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KEY WORDS: Automated colorimeter, cottonseed oil, Lovibond, visual color, Wesson method.

Color is an important quality parameter of edible oil, both during and after the refining process. It is also frequently monitored for the condition of used oil. Sometimes, color in oil is used as the basis for its acceptance or rejection in the trade. Due primarily to its polyphenolic pigments, gossypol, and gossypol-like compounds, cottonseed oil is generally dark in color and difficult to refine consistently to the desired color (1). Thus, cottonseed oil color is clearly specified in the trading rules that have been established by the National Cottonseed Products Association (2). For example, prime crude cottonseed oil should not exceed 7.6 American Oil Chemists' Society (AOCS) red after caustic refining, and prime bleachable summer yellow cottonseed oil should be bleachable to less than 2.5 AOCS red (2).

Lovibond color of oil is an arbitrary scale and the most widely used in the edible oil industry (3). It is a visual comparison method, measured with a colorimeter equipped with a set of colored glasses designed according to either British Lovibond Color Scale (Lovibond Scale) or AOCS Tintometer Wesson Color Scale (AOCS Scale). Lovibond Color Standards and AOCS Tintometer Color Scale or Wesson Method are described in the *Official Methods and Recommended Practices of the American Oil Chemists' Society*, Cc 13e-92 and Cc 13b-45, respectively (4). The Lovibond method, Cc 13e-92, uses a Model E Lovibond Tintometer and red, yellow, blue, and neutral glasses to match the oil color and is practiced primarily outside of the United States. The Wesson method, published as AOCS Method Cc 13b-45 in 1945 (4,5), uses an AF710 AOCS Tintometer to match the oil color with red and yellow colored glasses.

These methods are accurate but require an experienced observer to achieve the desired reliability and repeatability. With approximately 8% of males and 0.4% of females suffering from varying degrees of color blindness, the potential to have an operator with defective color vision is rather high (3). To eliminate operator variability, attempts to develop an instrument to replace the visual color measurement have been made. A collaborative effort in the late 1940s (6) led to the development of an official spectrophotometric color method, Cc 13c-50 (4), which uses matched glass cylindric cuvettes of approximately 21.8 mm i.d. and calculates a value for red color based on absorbance measurements at 460, 550, 620, and 670 nm. This method showed good correlation ($r^2 = 0.993$) with the red color determined by the visual AOCS Wesson method (Cc 13b-45) and is a potential alternative to the manual Lovibond method (7). The spectrophotometric method is seldom used (8).

In recent years, automated colorimeters have become available, primarily from Tintometer Ltd. (Salisbury, England) (3). Initial collaborative efforts to correlate the automatic Tintometer Model AF960 with the manual Tintometer Model AF710 did not produce a final conclusion or recommendation (9). The present work was done to assess the feasibility of using Colourscan, a personal computer-based colorimeter, to replace the visual method or manual Tintometer AF710 for refined and bleached cottonseed oils with a cell of 133.4-mm (5 1/4-in) light path. At the same time, the correlation between AOCS-Red and light-path lengths for refined cottonseed oil was also studied with the Colourscan.

EXPERIMENTAL PROCEDURES

Eleven crude cottonseed oil samples and four factory-refined oils were supplied by five different oil mills in the United States during the 1993 crushing season. Crude oils were re-

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fined by a commercial lab according to AOCS Method Ca 9e-52 (4). All refined oils were then bleached by the same commercial lab according to AOCS Method Cc 8a-52 (4). Visual color measurements of these fifteen refined oils and thirteen bleached oils plus two duplicate refined oils were made by two commercial laboratories and two factory laboratories. One factory provided two sets of visual color readings by two experienced professionals. All visual color measurements were done by AOCS Method Cc 13b-45 (4) with a Tintometer Model 710 (The Tintometer Ltd.) in a 133.4-mm (5 1/4-in) sample glass tube. Automated color readings of the same set of refined and bleached cottonseed oils were taken from a personal computer-based Colourscan (The Tintometer Ltd.) immediately before or after their visual color values were measured. All oils were examined in a cell of 133.4-mm (5 1/4-in) light path. Cells with various light paths were also available with the Colourscan. Initial tests showed no temperature effect on the color readings of cottonseed oil in the Colourscan between ambient temperature and 60°C. All readings in the Colourscan were carried out at 30°C to prevent solidification of cottonseed oil.

Least-square linear regression was applied to each set of visual color values vs. the automated color readings that were closest in time to the visual measurements. The errors of their slopes and intercepts were also assessed at 95% confidence level.

RESULTS AND DISCUSSION

A set of refined and bleached cottonseed oils plus two replicate samples (28 oil samples) were read by an automated colorimeter, Colourscan, and by two commercial lab chemists and four plant chemists. As defined in AOCS Method Cc 13b-45 (4), yellow is fixed at ten times red when oil color is less than 3.5 red and at 35 when oil color is more than 3.5 red. Thus, few chemists attempted to take the effort to visually match yellow color for cottonseed oils. Although the automated colorimeter tirelessly assigned yellow color to each oil sample, due to the fixed selection of yellow for visual color measurement, it is meaningless to correlate the yellow readings from these two different methods. Therefore, only the red color of visual measurements, according to AOCS Method Cc 13b-45 (4) and the AOCS color scale red from Colourscan are presented. These results are listed in Table 1 and shown in Figure 1. For the replicate samples, Colourscan gave nearly perfect reproducibility, while the visual readings were reproduced by ±0.1 to 0.2 unit of the AOCS red scale.

TABLE 1
Red Color of Refined and Bleached Cottonseed Oils by Colourscan and Visual Method in AOCS Color Scale

Source of data	Colourscan AOCS-red[a]	Commercial Lab #1[b]	Commercial Lab #2[b]	Colourscan AOCS-red[a]	Plant #1[b]	Plant #2[b] Technician 1	Plant #2[b] Technician 2	Colourscan AOCS-red[a]
Date	December 2–3/93	December 7/93	December 14/93	December 16–17/93	December 20/93	December 30/93	January 2/94	January 10/94
Refined oils								
R01	7.9	8.0	7.1	7.8	0.0	7.3	7.5	7.3
R02	8.1	8.6	8.5	8.2	9.0	8.8	8.8	7.9
R03	7.0	7.3	7.0	7.3	7.6	7.1	7.5	7.0
R04	9.7	10.4	7.9	9.4	10.0	10.1	9.9	9.1
R05	9.0	9.7	8.4	8.8	9.0	8.9	9.2	8.4
R06	10.6	10.7	8.1	9.7	10.0	10.0	10.2	9.4
R07	9.0	9.8	8.2	8.8	10.0	9.1	9.5	8.4
R08	10.9	9.8	7.8	9.4	10.0	9.0	9.1	9.0
R09	12.1	12.5	9.2	11.5	13.0	11.9	12.0	11.1
R10	5.9	6.0	5.2	5.9	7.6	6.2	6.5	5.8
R11	5.9	6.2	4.7	5.8	6.0	6.2	6.2	5.9
R11-Dup.	5.9	6.2	5.1	5.9	6.0	6.1	6.5	5.9
R12	5.6	5.9	4.9	5.6	5.5	5.9	5.8	5.4
R13	4.6	5.1	3.6	4.6	4.1	4.7	4.7	4.5
R14	3.9	4.0	3.3	3.9	4.0	3.7	3.7	4.0
R14-Dup.	3.9	3.9	3.3	3.9	4.1	3.6	3.8	3.8
R15	4.0	4.1	3.5	4.1	4.0	4.2	4.2	4.0
Bleached oils								
B01	3.4	3.7	2.1	3.3	3.0	3.6	3.8	3.2
B02	3.6	3.7	3.0	4.1	3.5	3.2	3.3	3.9
B03	2.6	2.3	2.1	2.7	2.5	2.5	2.5	2.6
B04	4.1	4.1	3.1	3.8	3.0	4.0	3.8	3.8
B05	4.1	4.2	3.3	4.1	4.0	4.3	4.0	3.9
B06	3.4	3.5	3.1	3.3	2.5	3.1	3.5	3.3
B07	3.1	3.1	2.2	3.1	3.0	3.4	3.0	3.1
B08	4.3	4.2	3.1	4.1	3.0	4.0	3.6	3.9
B09	5.0	5.3	3.8	4.7	4.0	4.7	4.6	4.5
B10	3.0	2.9	2.1	2.9	3.0	3.1	3.0	2.6
B11	2.0	2.0	0.9	1.9	2.5	1.7	2.1	2.0
B12	1.4	1.4	1.0	1.4	2.0	1.3	1.3	1.4
B13	1.2	1.3	0.9	1.4	2.0	1.3	1.2	1.2
B13	1.2	1.3	0.9	1.4	2.0	1.3	1.2	1.2

[a]Colourscan AOCS red color was read from oil in a 133.4-mm (5 1/4-in) cell at 30°C.

[b]Commercial and plant labs measured oil color in a 133.4-mm (5 1/4-in) glass tube with a Tintometer AF710 (The Tintometer Ltd., Salisbury, England) according to AOCS Method Ca 13b-45 (Ref. 4).

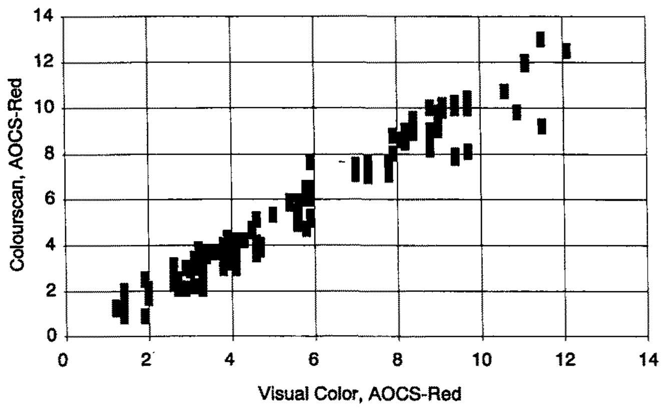

FIG. 1. Colourscan AOCS-red vs. visual AOCS-red for refined and bleached cottonseed oils.

Results of least-square linear regression analysis of the data from Table 1 are given in Table 2. For each set of data from refined and bleached oils, the visual color values correlated well with automated color readings, with r^2 values ranging from 0.96 to 0.99. Refined oil samples had r^2 values of 0.93 to 0.99. Lighter-colored bleached oil samples had slightly lower r^2 values than those of refined oils. Results from the lab of Plant #1 had the worst r^2 value (0.79) for bleached oils, and it was later confirmed that the professional who read the bleached oil samples has a mild color vision defect. If we discount this special case, most of the correlation slopes and intercepts are close to their corresponding theoretical values of 1 and 0. This is supported by the error estimates of these slopes and intercepts, which are not significantly different from 1 and 0 at 95% confidence level. When all the data sets were combined, a total of 150 pairs of visual vs. Colourscan readings, a near-perfect correlation was obtained, with a slope >0.999, constant = 0 and $r^2 = 1$.

Two different models (Colourscan and Tintometer PFX 990) of automated colorimeter are already being used in various labs. To verify the performance of Colourscan, three unlabelled standard color glass filters with red scale ranging from 0.4 to 4.0 were sent to labs that have an operating Colourscan. Because the automated colorimeter can measure color according to either Lovibond or AOCS color scale, both results are displayed in Table 3. Results obtained from three different labs for the same set of color standards agreed within 0.1 unit of red and 0.4 to 1.0 unit of yellow in the Lovibond scale; slightly greater deviations were observed in AOCS color scale, 0.06 to 0.15 unit of red and 0.3 to 2.77 units of yellow. These results indicate that the automated color instruments are performing relatively consistently.

A good linearity between Colourscan red color of refined cottonseed oil and cell length from 133.4 to 2.5 mm was observed. The results are shown in Figure 2. Good correlations, with r^2 of 0.997 for AOCS Color Scale and 0.988 for Lovibond Color Scale were established. However, close examination of the data showed a slight increase in slope for the following three ranges of cell pathlength: 133.4 to 50.8 mm, 50.8 to 12.7 mm, and 10 to 2.5 mm. The reason for this characteristic of pathlength is unclear. For oils darker than once-refined cottonseed oil, such as poorly or improperly refined oils, a noticeable concave upward curvature of the Colourscan red vs. light path was observed. This phenomenon may be explained by the dichroism properties of darker oils (10). In this case, the natural logarithm of either color scale showed a near linear relationship with light pathlengths. The multiple choices of cell length permitted the color of dark oils, including crude cottonseed oils, to be studied or monitored by the automated colorimeter.

This pilot study demonstrated that an automated colorimeter, such as Colourscan, can be used effectively to replace AOCS visual color measurement for cottonseed oils. Its sensitivity and reproducibility at ±0.1 unit of red should be adequate at the present time for the study of oil quality in terms of its color appearance. The automated colorimeter is repro-

TABLE 2
Visual Color vs. Colourscan for Refined and Bleached Cottonseed Oils

Lab number		Refined only		Bleached only		Refined and bleached	
		Mean	Error[a]	Mean	Error	Mean	Error
Comm. #1	Intercept	0.36	0.83	−0.10	0.30	0.02	0.29
	Slope	0.99	0.10	1.04	0.09	1.02	0.05
	R-square	0.97		0.98		0.99	
Comm. #2	Intercept	−0.60	1.10	−0.41	0.54	−0.45	0.40
	Slope	1.14	0.14	0.88	0.16	0.93	0.07
	R-square	0.96		0.93		0.97	
Plant #1	Intercept	0.14	1.12	1.24	0.61	−0.46	0.53
	Slope	0.86	0.15	0.53	0.19	1.11	0.09
	R-square	0.93		0.79		0.96	
Plant #2A	Intercept	−0.33	0.60	−0.04	0.69	−0.20	0.27
	Slope	1.10	0.08	1.03	0.22	1.08	0.05
	R-square	0.99		0.91		0.99	
Plant #2B	Intercept	−0.27	0.56	0.14	0.61	−0.28	0.26
	Slope	1.11	0.08	0.96	0.19	1.11	0.04
	R-square	0.99		0.92		0.99	

[a]Error = t × standard error at 95% confidence interval. Comm., commercial.

TABLE 3
Performance Evaluation of Colourscan with Standard Color Glasses

Standard	#1		#2		#3	
Lovibond	Red	Yellow	Red	Yellow	Red	Yellow
Lab #1	0.4	4.2	2	13.9	4	50
Lab #2	0.4	4.3	2	14	4	48
Lab #3	0.6	4.4	2	14.2	4.1	50
Lab #4	0.4	4.2	2	14	4	50
Average	0.45	4.28	2.00	14.03	4.03	49.50
Standard deviation	0.10	0.10	0.00	0.13	0.05	1.00
% Standard deviation	22.22	2.24	0.00	0.90	1.24	2.02
AOCS	Red	Yellow	Red	Yellow	Red	Yellow
Lab #1	0.4	5	1.8	16.3	3.5	57.6
Lab #2	0.4	5.3	1.8	16.7	3.6	57.6
Lab #3	0.5	5.6	1.6	18.1	3.3	62.4
Average	0.43	5.30	1.73	17.03	3.47	59.20
Standard deviation	0.06	0.30	0.12	0.95	0.15	2.77
% Standard deviation	13.32	5.66	6.66	5.55	4.41	4.68

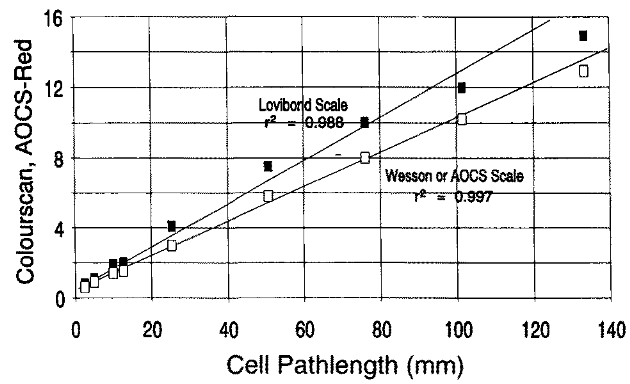

FIG. 2. Colourscan AOCS-red of refined cottonseed oil vs. cell path length.

ducible and easy to operate without the concern of operator variability in reading visual color. The initial capital investment, however, might be a barrier to its broad application. When the automated colorimeter becomes more affordable and proper correlation with the variety of oil types is established, the automated color measurement may be recommended for use in AOCS methods for color.

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