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SIMPLIFIED APPARATUS FOR TECHNICAL SUGAR COLORIMETRY[1]

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ABSTRACT

The apparatus consists of a Duboscq colorimeter and an incandescent light source with suitable spectral filters and glass photometric standards for the measurement of absorbancy in sugar solutions. The absorbancy of all except very pale solutions, may be determined at 560 mμ by using a special yellow-green filter. Solutions of high-grade sugar products having little color are treated as a special case, and using a blue filter, measurements are made at 460 mμ. The results obtainable are satisfactory for technical purposes.

CONTENTS

I. INTRODUCTION

The value of methods of sugar colorimetry based upon spectrophotometry or the measurement of light absorbed by sugar solutions at definite wave lengths is well recognized. The general adoption of such methods for routine factory purposes has been delayed chiefly because adequate instruments, of which there are several, are considered too complicated, too delicate, or too expensive. It is possible, however, to obtain satisfactory results by means of abridged methods and with inexpensive apparatus.

What is perhaps the first attempt at simplification resulted in the apparatus devised by Bates and associates,[2] which consists of a Stammer colorimeter with a rotating sectored disk of known transmission fitted under the open tube to serve as a photometer. With mercury-arc illumination, and with appropriate spectral filters at the eyepiece, the transmittancy of sugar solutions is measured at wave

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[1] Parts of this article were read before the Division of Sugar Chemistry at various meetings of the American Chemcial Society, as follows:
Glass Standards and the Duboscq Instrument in Sugar Colorimetry, Buffalo, N. Y., August 1931.
A Color Filter for Visual Sugar Colorimetry, Washington, D. C., March 1933.

[2] (Abstract), Int. Sugar J. **22**, 654 (1920).

lengths 435.8, 546.1, and 578 mμ. The same kind of photometric device and illumination is adaptable to other types of the Duboscq colorimeter. By interpolation between data obtained at 546.1 and 578 mμ, Peters and Phelps[3] later showed that the specific absorptive index at 560 mμ may be calculated with sufficient accuracy for technical purposes, $-\log \mathbf{t}$ at 560 mμ having been shown to be a nearly correct estimate of color in sugar products.[4]

A further step in simplification, as described in the present paper, results from the use of a filter that isolates a narrow spectral band at 560 mμ, permitting the direct determination of $-\log \mathbf{t}$ at this wave length with ordinary incandescent tungsten illumination. Another filter with optical centroid at 460 mμ is recommended for nearly colorless solutions. These filters may be employed with any suitable photometric device such as the Hess-Ives, the Pulfrich, the Martens photometer, or the modified Stammer referred to above.

With the idea of employing readily available and well known equipment in the present case, a standard type of Duboscq colorimeter was used as the comparator. Glass plates calibrated for transmission at one or both wave lengths served as photometric standards.

II. SPECTROPHOTOMETRIC TERMINOLOGY

Spectrophotometric terminology as relating to sugar solutions was published by Peters and Phelps[5] in complete form under the title Color Nomenclature in the Sugar Industry, in which the recommendations of the Committee on Spectrophotometry of the Optical Society of America[6] were strictly followed insofar as they adequately covered the ground. Since these publications are no longer readily available it is considered necessary to repeat here such definitions as apply directly to the methods to be described.

In the case of light, homogeneous with respect to wave length, incident upon a transparent, nondiffusing solid with plane parallel faces such as a polished glass plate

T = transmission, the fraction of light that gets through and is not reflected at the surfaces nor absorbed by the solid. T may also refer to the transmission of a cell with parallel glass end plates.

In the case of solutions contained in cells with parallel glass end-plates

$T_{\text{sol.}}$ = the transmission of a given cell containing solution.

$T_{\text{sov.}}$ = the transmission of the same or another similar cell containing the solvent.

$\mathbf{T}=\frac{T_{\text{sol.}}}{T_{\text{sov.}}}$ = transmittancy, the transmission after correction for reflection at the surfaces and the absorption, if any, by the solvent.

$-\log \mathbf{T}$ = absorbancy (of solutions).

$\mathbf{t}$ = specific transmissivity = transmittancy reduced to unit conditions regarding thickness and concentration.

b = thickness (in centimeters) of absorbing medium.

c = concentration (gram sugar dry substance per 1 ml solution).

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[3] BS J. Research **2**, 335 (1928) RP38.

[4] Tech. Pap. BS **21**, 267 (1927) T338.

[5] Tech. Pap. BS **21**, 261 (1927) T338.

[6] J. Opt. Soc. Am. and Rev. Sci. Instr. **10**, 169-241 (1925).

$\mathbf{t}=\sqrt[bc]{\mathbf{T}}$, or $-\log \mathbf{t}=\frac{1}{bc}(-\log \mathbf{T})$=Lambert-Beer law to which sugar solutions and caramel conform.

$-\log \mathbf{t}$, the specific absorptive index, is the absorptive index of a solution reduced to unit conditions regarding thickness and concentration. It is a measure of the coloring or light-absorbing power of the unknown amount of coloring matter associated with 1 g of sugar dry substance.

λ=wave length.

mμ=millimicron=meter$\times 10^{-9}$, a measure of λ.

III. COLORIMETERS

A Bausch and Lomb Duboscq colorimeter with 10 cm-scales, as illustrated in figure 1, permits the determination of transmittancies ranging from less than 10 to above 90 percent. In some colorimeters, depending upon their construction, the half-fields do not match, as they should, when scale readings are too widely separated. In the present instrument, with distilled water in the cups, it was found that the half-fields match at a difference in scale reading as great as 8.5 cm, affording a sufficient range. The illuminating mirror is glass, with the under surface silvered and the outer surface ground. The inclined eyepiece, as already offered by some manufacturers, is a feature to be recommended. In this case the inclination was accomplished by introducing a 60° prism in a suitable housing in the telescope tube. To support the glass photometric standard, a brass shelf, with heavy bracket, is rigidly fastened with two screws to the vertical column, leaving a clearance of 1 cm between the shelf and the lowest position of the cup stages. The two orifices of the shelf centered below the cups are 25 mm in diameter. A plate carrier with a 25-mm orifice, over which the standard is placed, slides between guides on the shelf. A stop at the center of the shelf engages in a slot in the carrier and serves to center the orifices under either stage when the carrier is moved from side to side.

Some Duboscq instruments have an open space between the top of the plungers and the rhombs in which the standard may be inserted and the shelf is then unnecessary. Whatever the construction of the instrument, provision is to be made for easy change of standards from one side to the other.

A Klett colorimeter with short cells allowing a useful range of about 5 cm has given good results. Satisfactory results were not obtained when the long cells were used. A pair of extra stages mounted below the cells supported the standards.

IV. SPECTRAL FILTERS

1. FOR 560 MILLIMICRONS

Two filters have been devised that are suitable for the measurement of absorbancy in sugar solutions at 560 mμ, with incandescent tungsten illumination, one by the writer [7] and a later one by Gibson.[8] The composition [9] of these filters is as follows:

Brewster		Gibson	
Material	Thickness	Designation of glass	Thickness
			mm
Wratten filter 21	1 layer	Corning 351	4.55
Wratten filter 61	1 layer	Corning didymium	5.82
Corning didymium glass	6.5 mm	Jena VG–3	1.99
Colorless glass	1 to 2 mm	Jena BG–18	1.94

The components are sealed together with canada balsam and the edges may be bound with black tape. The colorless glass in the Brewster filter serves to protect the gelatin film. Transmission curves of these filters are shown in figure 2. For the writer's filter the spectral centroid of the transmitted light for incandescent tungsten illumination at 2,848° K is 558.8 mμ. There is slight leakage of light between 600 and 630 mμ and between 680 and 700 mμ, but this has little or no effect upon the results. The dyed gelatin components are stable for at least one year and are easily renewed.

For Gibson's filter the spectral centroid of the transmitted light for tungsten at 2,848° K is given as 560.0 mμ. Advantages of this filter over the older one are: (1) optical permanence, (2) the location of the spectral centroid exactly at 560.0 mμ, (3) the higher transmission at 560 mμ, and (4) the higher ratio of height to width of its transmission curve. Before publication of his description, Dr. Gibson kindly placed his filter at the writer's disposal for trial in sugar colorimetry, some results of which are included in a later section. Either filter is capable of yielding satisfactory results in sugar colorimetry, and for convenience may be of such size as to fit in the eyepiece tube of the colorimeter and rest upon a diaphragm or the lower lens mounting.

2. FOR 460 MILLIMICRONS

Highly desirable as it may be that all measurements be made at 560 mμ, this is a matter of considerable difficulty in the case of very pale solutions, such as those of highest-grade refinery products, where special arrangement must be made for liquid columns long enough to provide measurable absorption, regardless of what type of instrument is being used. At the shorter wave lengths in the blue and violet where absorption caused by yellowish coloring matter is greater,

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[7] J. F. Brewster, (Abstract), Facts About Sugar, **28,** 228 (1933).

[8] K. S. Gibson, J. Research NBS **14,** 545 (1935) RP785; J. Opt Soc. Am. **25,** 131 (1935).

[9] The materials composing these filters are described in advertising booklets as follows:
Wratten filters, Eastman Kodak Co., Rochester, N. Y.
Glass color filters, Corning Glass Works, Corning, N. Y.
Jena Colored Optical Filter Glasses For Scientific and Technical Purposes, obtainable from Fish-Schurman, Inc., 230 East Forty-fifth Street, New York, N. Y.

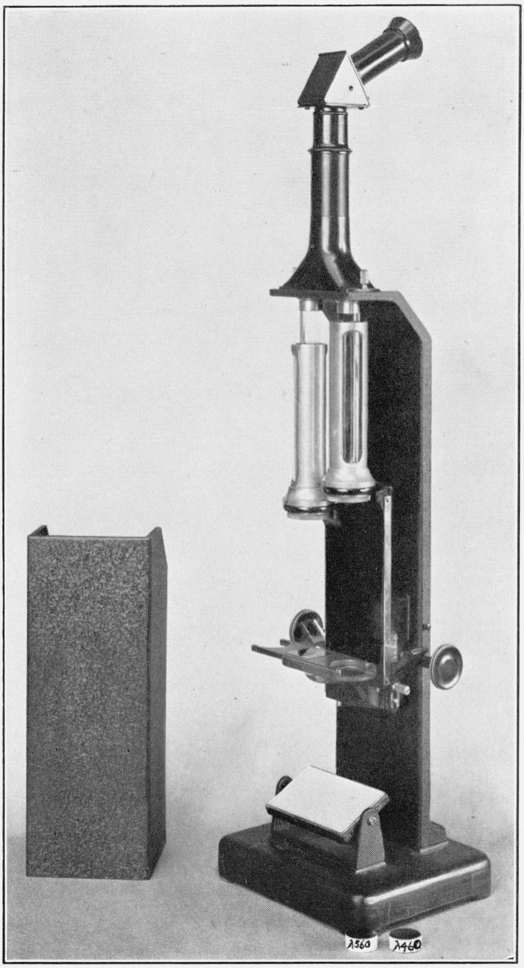

FIGURE 1.—*Duboscq colorimeter for measurement of sugar color, showing inclined eyepiece, mounting of the glass standard, and spectral filters.*

shorter columns may be used (see uppermost curve, fig. 3). In consideration of the relative visibility of light and ease of matching field intensities (see curve V, fig. 2) it is preferable to use the longest wave length in this region compatible with sufficient absorption by the sample. The filter chosen for this purpose consists of a single blue glass designated as Jena BG–12.[10] The thickness is 3.42 mm. The spectral centroid of the band transmitted by this filter for incandescent tungsten at 2,848° K is 459.9 mμ, and the transmission at 460 mμ is 0.294. No advantages accrued by reducing the width of the transmitted band by various means. The transmission curve of this filter is shown in figure 2. The small dotted curve at the bottom of the chart gives a comparison of the visibility of the energy transmitted by this filter as against that by the two 560 mμ filters.

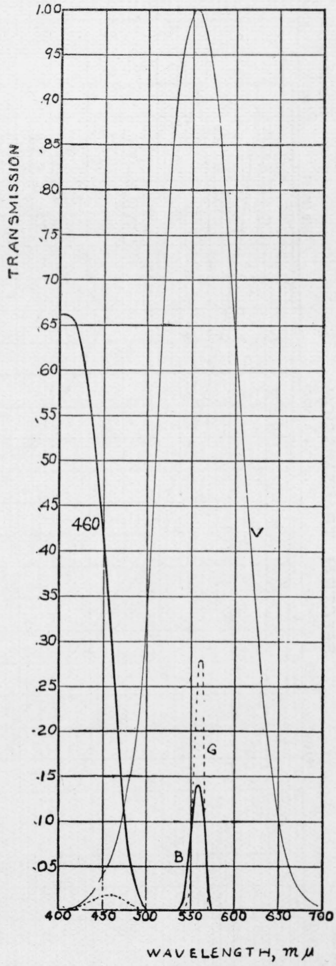

FIGURE 2.—*Transmission of spectral filters.*

460=Jena BG–12, 3.42 mm thick; G=Gibson filter for 560 mμ; B=Brewster filter for 560 mμ; V=relative visibility of radiant energy.

Although colored glasses may not be precisely reproducible in spectral transmission from one melt to another, it is believed that any differences will be too small to cause a serious shift of the spectral centroid, particularly in the case of the Jena BG–12 glass, if the deviation from the specified thickness is not greater than 0.02 or 0.03 mm.

V. GLASS PHOTOMETRIC STANDARDS

For the colorimetry of darker sugar products, polished plates of carbon amber glass, calibrated in terms of transmission at 560 mμ, are used as comparison standards. This glass is produced in various shades ranging from dark amber to pale yellow.[11] By reference to figure 3, spectral-transmission curves (percent T at λ) of some of these glasses may be compared with similar curves for caramel preparations, the caramel in either case being so diluted that in a 1-cm layer at 560 mμ, **T** is approximately equal to T of the respective glass. The similarity in the slope of each pair of curves in the spectral region 440 mμ to about 600 mμ, which includes the bands inclosed by the filters, is to be noted. Due to this similarity, it is possible to obtain a good chromaticity match in this region between glass and a sugar solution with filters that include rather wide spectral bands. From 600 to 700

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[10] See footnote 9.

[11] The writer desires to express his thanks to Dr. E. D. Tillyer, American Optical Co., Southbridge, Mass., for supplying specimens of amber glass and for information concerning them.

mμ the curves diverge, the caramel having an increasingly higher transmission than the glass for the orange and red, so that when compared under ordinary conditions of incandescent illumination, the sugar color appears more red than the glass and an accurate match of intensities is difficult. This is the familiar defect of the Stammer method. However, since the spectral centroid of light transmitted by a combination of sugar solutions and a filter of broad spectral range shifts with change in concentration of sugar coloring matter, the use of filters transmitting only a narrow spectral band is imperative for accurate results.

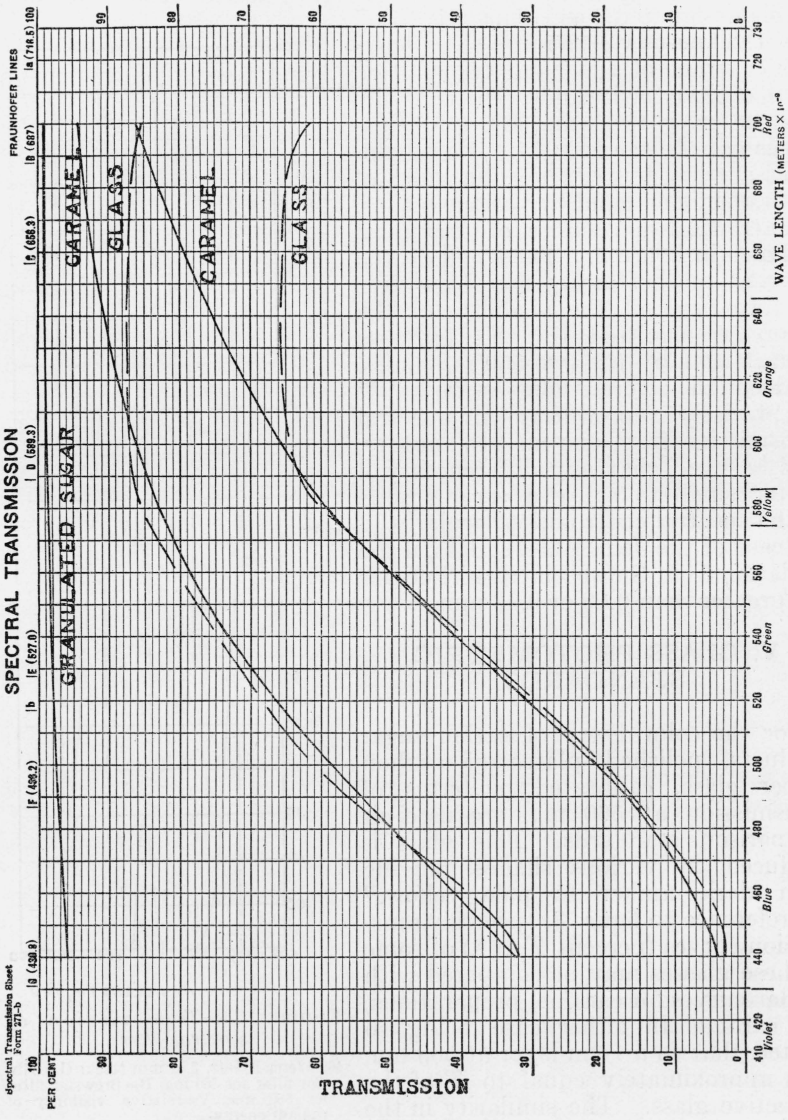

FIGURE 3.—*Comparison of the spectral transmission of aqueous caramel preparations and amber glasses.*

Standard plates in three shades of amber glass are a sufficient number for the colorimetry of products ranging from the darkest that may be read, up to and including off-color granulated sugar. It is recommended that the transmission of these plates, controlled by shade and thickness of glass, be close to 0.50, 0.70, and 0.80, respectively. Since the plates are to be calibrated independently, it is unnecessary in purchasing to specify a transmission tolerance closer to these values than ± 0.02, a condition easily attained in their manufacture. The glass is customarily supplied in 2-inch polished squares, free from imperfections and with satisfactory parallelism of faces. Other sizes and shapes may be specified to conform to the construction of the instrument.

Stammer plates, unless previously calibrated, are worthless for the present scheme, or any other scheme of sugar colorimetry, because of possible variation in transmission among them, not only at 560 mμ, but over the entire visible spectrum, as has been shown by Spengler and Landt.[12]

For the colorimetry of very pale solutions, a calibrated plate of colorless optical glass may be used. The optical density of such glass is due principally to reflection at the surfaces rather than to absorption, and, in good specimens, the transmission at 560 and 460 mμ is the same within the limits of observational error, so that the calibration value as determined for 560 mμ may be adopted for 460 mμ.

For high accuracy, glass plates to be employed as photometric standards should be sent to the National Bureau of Standards for calibration. With one such standard so calibrated, however, it is possible, as described later, to calibrate others that are suitable for working standards in cases where extreme accuracy is unnecessary.

VI. METHOD OF OBSERVATION AND CALCULATION OF RESULTS

Since Beer's law does not hold for turbid sugar solutions these are to be rendered transparent by filtration through asbestos, as described elsewhere.[13] The Brix of the solution, which should be 60.0 or higher, is determined preferably by a refractometer, and the dry substance, c, in grams per milliliter is found by calculation, thus,

$c=\frac{\text{Brix}\times\text{true density (Plato)}}{100}$, or more conveniently by reference to the density table of Brewster and Phelps.[14] A portion of the solution is added to each colorimeter cup and with the appropriate filter in place at the eyepiece the zero setting is checked. Since a perfect zero setting is not easily attained, compensation is made for this error, and for any others due to asymmetry of the instrument by a transposition method as follows:

A standard plate is centered under one of the cups, the corresponding scale set to a definite "blank" reading, say 0.5 or 1.0 cm, and five readings taken in the usual manner. The plate is now centered under the opposite cup, the same blank scale reading set above it, and another series of five readings taken.

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[12] Z. Ver. deut. Zucker Ind. **83,** 223 (1933).

[13] BS J. Research **10,** 365 (1933) RP536. See also Tech. Pap. BS **21,** 261 (1927) T338.

[14] See page 370 of BS J. Research **10,** (1933) RP536.

The mean of the ten readings, minus the blank setting, expressed in centimeters gives the depth b of liquid for which $\mathbf{T}$[15] of the solution $=T$ of the standard plate as given by calibration. The value of $-\log \mathbf{T}$ is found by reference to log tables or to the convenient colog table given by Peters and Phelps.[16] The data are substituted in the Beer's law equation, $-\log \mathbf{t}=\frac{1}{cb}(-\log \mathbf{T})$. The results may be expressed as $-\log \mathbf{t}_{560}$, or $-\log \mathbf{t}_{460}$, depending upon the filter used.

The following example of the determination of $-\log \mathbf{t}$ at 560 mμ in the case of a solution of washed raw sugar is an illustration:

Refractometric Brix, 60.9, corresponding to true density, 20°, 1.29176.

$$c=\frac{60.9\times 1.29176}{100}=0.7867$$

Standard plate, $T=0.579$ or $-\log T=0.2373$.

Photometric measurements:	cm.
Right scale, mean of 5 settings	3.332
Left scale, mean of 5 settings	3.028
Mean of 10 settings	3.180
Subtracting blank setting	1.000
	$b=2.180$

Substituting in the Beer's law equation

$$-\log \mathbf{t}=\frac{0.2373}{2.18\times 0.7867}=0.1384.$$

The calculation of results is simplified by using a slide rule with reciprocal scales.

VII. COMPARATIVE RESULTS

To gain an idea of the reliability of the present method, some results obtained with the Duboscq colorimeter and a Bausch and Lomb spectrophotometer may be compared by reference to tables 1, 2, and 3. The spectrophotometer is controlled by means of known wave-length and transmission standards and is capable, particularly in the case of amber glass or solutions at 560 mμ, of yielding results in error by considerably less than 1 percent of the transmission. Differences or errors in the final results are cumulative and attributable to both instruments.

In table 1 are given results of measurements of $-\log \mathbf{t}$ at 560 and at 460 mμ in the case of solutions of sugars. Sugar 1, column 1, was a washed Cuban raw; 2, 3, and 4 were solutions made by diluting sample 1 with colorless sirup; 5, 6, and 7 were granulated sugars; and nos. 8 and 9 were tablets and confectioners crystals, respectively. Measurements were made on portions of each solution with the colorimeter and with the spectrophotometer. Column headings 1 to 8 will be understood from the description of the method as given in the preceding section. In columns 9 and 10 the differences, D, in $-\log \mathbf{t}$ and $\mathbf{t}$ as found with the two instruments are expressed as the percentage of the spectrophotometric values.

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[15] Strictly the quantity measured is the transmittance. However, since the absorption by the solvent, water, is negligible in the thicknesses used, the transmittance and the transmittancy are numerically equal, and the symbol $\mathbf{T}$ is used in the present discussion, since it is the quantity ordinarily determined with the spectrophotometer for which the proposed apparatus is a substitute.

[16] Tech. Pap. BS **21**, 261 (1927) T338.

TABLE 1.—*Determination of* $-\log \mathbf{t}$ *in sugar solutions*

DUBOSCQ COLORIMETER					SPECTROPHOTOMETER				
1	2	3	4	5	6	7	8	9	10
Sugar	c, g/ml	b, cm	$-\log T$	$-\log \mathbf{t}$	b, cm	$-\log \mathbf{T}$	$-\log \mathbf{t}$	D, %, $-\log \mathbf{t}$	D, % t
560 mμ—BREWSTER FILTER									
1	0.79330	1.182	0.2373	0.25307	2	0.39794	0.25081	+0.90	−0.52
2	.78668	2.180	.2373	.13837	2	.21896	.13916	−.06	+.13
3	.79496	4.461	.2373	.06691	2	.10513	.06612	+1.20	−.69
4	.79165	7.274	.2373	.04121	5	.16494	.04167	−1.10	+.52
5	.79662	6.909	.03245	.00589	12	.05502	.00576	+2.25	−.21
6	.79496	6.224	.03245	.00656	12	.06298	.00660	−0.61	.00
460 mμ FILTER									
7	.8083	1.705	.03953	.0288	12	.29158	.03050	−5.58	+0.43
8	.7966	6.999	.03953	.00709	12	.07058	.00733	−3.27	+.47
9	.8033	7.707	.03953	.00639	20	.09864	.00608	+4.93	−.11

In table 2 are given results of measurement of $-\log \mathbf{T}$ at 560 and 460 mμ in the case of some caramel preparations. For the measurements at 560 mμ the darkest preparation designated as 100 in column 1 was analyzed with the Duboscq colorimeter and the spectrophotometer, the results given in the first two lines being practically identical. The preparation was then diluted volumetrically with water to contain the volumes, in percent, of the original that follow in column 1. The remaining four solutions of this series were not analyzed with the spectrophotometer, but the calculated values for $-\log \mathbf{T}_{1\,\text{cm}}$ are percentages of original $-\log \mathbf{T}_{1\,\text{cm}}$ corresponding to the dilution. In the 460 mμ series all of the caramel preparations were analyzed with both instruments. In columns 2, 3, and 4 are given, respectively, depth b, as found with the colorimeter; $-\log T$ of the glass standard; and $-\log \mathbf{T}_{1\,\text{cm}}$ (values in column 3 divided by corresponding values of column 2). In column 5 the values of $-\log \mathbf{T}_{1\,\text{cm}}$ are calculated as percentages of the original corresponding to the concentrations in column 1. The experimental and calculated values of $\mathbf{T}_{1\,\text{cm}}$ appear in columns 6 and 7, respectively, and the differences as the percentage of the calculated values of $-\log \mathbf{T}_{1\,\text{cm}}$ and $\mathbf{T}_{1\,\text{cm}}$ in columns 8 and 9.

TABLE 2.—*Absorbancy and transmittancy of caramel preparations*

1	2	3	4	5	6	7	8	9
Conc. orig. prep. ml/100	b, cm	$-\log \mathbf{T}$	$-\log \mathbf{T}_{1\,\text{cm}}$ Found	$-\log \mathbf{T}_{1\,\text{cm}}$ Calculated	$\mathbf{T}_{1\,\text{cm}}$ Found	$\mathbf{T}_{1\,\text{cm}}$ Calculated	D, %, $-\log \mathbf{T}$	D, %, $\mathbf{T}$
SPECTROPHOTOMETER								
100	1.100	----------	0.61617	----------	0.242	----------	----------	----------
DUBOSCQ—BREWSTER 560 mμ FILTER								
100	0.366	0.22548	0.6160	0.6162	0.242	0.242	0.00	0.00
50	.734	.22548	.3072	.3081	.493	.492	−0.30	+0.20
25	1.501	.22548	.1502	.1540	.708	.702	−2.42	+.85
20	.996	.11919	.1196	.1232	.759	.753	−2.92	+.80
10	1.971	.11919	.0605	.0616	.870	.868	−1.79	+.23
DUBOSCQ—460 mμ FILTER								
----------	0.620	0.2660	0.4290	0.4220	0.372	0.378	+1.66	−1.25
----------	1.309	.2660	.2003	.2022	.630	.628	−0.94	+0.32
----------	4.048	.2660	.0657	.0648	.860	.861	+1.39	−0.12

VIII. CALIBRATION OF WORKING STANDARDS

The results obtained in the calibration at 560 mμ of some amber and colorless plates, as described below, are given in table 3.

The amber reference standard $T=0.703$ at 560 mμ, was calibrated by the colorimetry section of this Bureau. An aqueous preparation of caramel was made by diluting a small amount of a commercial product, available in the form of a thick tarry paste, so that a layer of solution 1 cm thick approximately matched the reference standard. Such dilute preparations fade slowly and are subject to infection with organisms. It was, therefore, used the same day it was prepared. With solution in both cups, and using a 560-mμ filter, a series of matchings (10 on each side) was made and the mean of the 20 readings taken to represent thickness b, of the layer wherein $\mathbf{T}=T$. Dividing $-\log \mathbf{T}$ by b gave $-\log \mathbf{T}$ for 1 cm thickness of caramel, which then was employed as a secondary standard. The data relating to this calibration appear as the first line of figures in table 3. The unknown plates were substituted, one by one, for the reference standard and matched against the caramel, giving the mean values for b in column 2. The value of $-\log \mathbf{T}_{1\,\mathrm{cm}}$ in column 3 multiplied by b gave $-\log T$, column 4, for each plate. The antilog T is given in column 5, which may be compared with the direct spectrophotometric value in column 6. The values of D in column 7 represent the percentage deviation from the spectrophotometric values. The last three calibrations with a Gibson filter, as indicated in table 3, were performed at a later time than the others. The average deviation, as expected, is smaller than with the older filter.

TABLE 3.—*Calibration of glass plates at λ 560*

1	2	3	4	5	6	7
Plate	b, cm	$-\log \mathbf{T}_{1\,\mathrm{cm}}$	$-\log T$	T Duboscq	T Spectrophotometer	D, % T
			BREWSTER FILTER			
Caramel	1.1885	0.12877	0.15304	----------	0.703	----------
3.54	1.7775	.12877	.2290	0.590	.589	+0.17
2.96	.9630	.12877	.1240	.752	.754	−.26
2.78	.9195	.12877	.1184	.761	.760	+.13
1.39	.5670	.12877	.0730	.845	.847	−.24
Colorless	.2380	.12877	.0306	.932	.928	+.43
			GIBSON FILTER			
3.54	1.940	0.1207	0.2341	0.583	0.585	−0.34
2.78	.9825	.1207	.1184	.761	.761	.00
Colorless	.2720	.1207	.03282	.927	.928	−.18

To reduce the probability of error in calibration the custom may be followed of taking the mean of a larger number of observations (at different times if necessary) and by more than one observer.

WASHINGTON, March 3, 1936.