

Status of Sugar Color and Turbidity Measurements

FRANK G. CARPENTER AND VICTOR R. DEITZ¹

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Introduction

Color has long been used in the sugar industry as a measure of a class of impurities. Although the word "color" in common usage connotes visual appearance, and some sugar technologists insist (9)² that this is what is meaningful, the ultimate interpretation of sugar color from a chemical viewpoint must be based on a measure of the amount of impurity that causes the visual appearance. Color is used both to monitor the sugar manufacturing or refining process, and to rate the final product at the consumer level. In both, the final interpretation is undoubtedly in terms of a measure of impurity. Even the housewife who looks at a yellowish trace of color interprets this (perhaps unconsciously) as a sure sign of less-than-pure sugar.

The distinction between visual appearance and the amount of impurity that causes the appearance is important because it influences the optical measurement and the method of expressing the results. The visual color is a three-dimensional entity that involves the entire visible spectrum and the response of the human eye. This measurement has had very limited acceptance by the sugar industry. The amount of impurity, on the other hand, can be related to the transmittance at one wave length and is a much less complex entity. The point of view taken in this paper is that the amount of impurities has more significance to sugar evaluation than does visual appearance. Accordingly, one object of this paper is to examine the factors whereby a measure of the amount of impurities can be gained from optical measurements on solutions.

However, since the word "color" will undoubtedly continue to be used to mean either visual appearance or amount of impurity in a very ambiguous manner, if a scale could be chosen that would be a good measure of amount of impurity and at least a fair indication of the visual appearance, then everyone would be happy, and a major source of confusion would be gone.

The sugar impurities which influence the optical measurement are of two classes, dissolved and suspended. Little is known of the composition of the suspensoids. They contain both high molecular weight organic and inorganic components, the latter being probably highly siliceous. Also, relatively little is known

¹ National Bureau of Standards, Washington, D.C.

² Numbers in parentheses refer to literature cited.

about the molecular composition and structure of the dissolved impurities. A large number of different colored compounds have been isolated in cane juice and raw sugar, but these account for only a small fraction of the total color.

Two fundamental optical measurements can be made in sugar solutions, absorption and scattering. Problems in interpretation arise when attempts are made to correlate these optical measurements with the non-sucrose constituents that are dissolved and suspended. The presence of strong chromophore groups in certain dissolved materials can strongly influence the absorption and large suspended or colloiddally dispersed particles contribute predominately to light scattering. Between these extremes are many materials for which this interpretation is not so distinct. Nevertheless, it is useful to divide the sugar impurities into two groups: a colorant fraction that contains the summation of all constituents that contribute to absorption, and a scattering material that has the corresponding light scattering behavior. This is an obvious simplification of the actual state of affairs, but it is pursued as a working hypothesis until a better method is required. Optical measurements obtained under a specified set of conditions will be used as a measure of the colorant and scattering material. The conditions will be chosen to provide the best measure of impurities and also for convenience, speed, ease, precision, or for any other good reason that arises, such as minimization of undesirable side effects.

Optical Properties of Sugar Solutions

When a light beam is passed through a solution, the transmittance is defined as the ratio of the transmitted flux to the incident flux, corrections, if any, for reflections and cell walls having already been made. Denoting the value of transmittance for solutions and solvent by $T_{\text{soln.}}$ and $T_{\text{solv.}}$ respectively, the transmittancy, T , is $T_{\text{soln.}}/T_{\text{solv.}}$. This solvent is properly sucrose and water at the same concentration as the solution. However, pure sucrose and water are both quite transparent in the ultraviolet, blue and yellow regions (230 to 700 $m\mu$). Water absorbs more than sucrose in the deep red (5). Therefore, for practical purposes, pure water makes a highly satisfactory reference solvent. It should be recognized, however, that the difference in refractive index between water and sugar solution will also have an important effect that will be discussed later. Transmittancy measurements constitute one class of primary data whereby the influence of the colorant and scattering material in sugar products may be studied.

In solutions containing light absorbing material only, the transmittancy is related to the cell depth, b , and to the concentration of colorant, c_i , by the familiar Lambert-Beer law,

$$-\log T_i = a_i bc_i$$

The constant of proportionality, a_i , is known as the absorbancy index (also, extinction coefficient) and this is a physical constant for a pure material. The subscript, i , refers to any one of the sugar impurities that absorb. Since the concentration or even the identity of these impurities is unknown, it is common practice in the sugar industry to define an "absorbancy index" as follows:

$$\frac{-\log T}{bc_s} = \frac{\sum a_i c_i}{c_s} = a_s$$

where c_s is the concentration of sugar. This terminology is incorrect inasmuch as a measure of the light absorbed by one constituent (impurity) is divided by the concentration of a different constituent (sugar). However, the value of a_s is proportional to the relative concentration of the colorant impurities to the concentration of the sugar ($\sum a_i c_i / c_s$) and this is precisely what the sugar technologist wants to know.

About ten years ago (5) it was pointed out that the colloidal materials in commercial sugar liquors contributed significantly by scattering to the transmittancy measurement. The term "attenuation index" (a^*) was proposed in order to distinguish a transmittancy measurement in which scattering was not negligible and this was expressed as:

$$\frac{-\log T}{bc} = a^*$$

The attenuation index is the sum of absorbancy index, a_s , and scattering index, s ,

$$a^* = a_s + s$$

In the absence of scattering,

$$\frac{-\log T}{bc} = a^* = a_s$$

In the absence of absorption,

$$\frac{-\log T}{bc} = a^* = s$$

Implicit in this concept is the independence of absorption and scattering. The scattering index, s , is related to the more familiar turbidity, τ , by the relation:

$$\frac{\tau}{2.3 c} = s$$

Turbidity may also be evaluated as the sum of the light scattered in all directions:

$$\tau = 2\pi \int_0^\pi R_\Theta \sin \Theta d\Theta,$$

where Θ is the angle of scattering and R_Θ is the Rayleigh ratio expressed as

$$R_\Theta = \frac{i_\Theta r^2}{I_0 V}$$

where r is the distance between the small scattering volume, (V), and the observer, i_Θ is the intensity of scattered light, and I_0 is the intensity of the incident light. The angular variation in the intensity of scattered light is expressed by a scattering envelope. Rieger and Carpenter (16) showed that these envelopes for sugar liquors (see Figure 1) were dominantly forward and of a similar shape. This similarity in shape, which has been thoroughly established, permits the estimate of the entire scattering envelope from a measurement at any one angle. Thus, the total turbidity

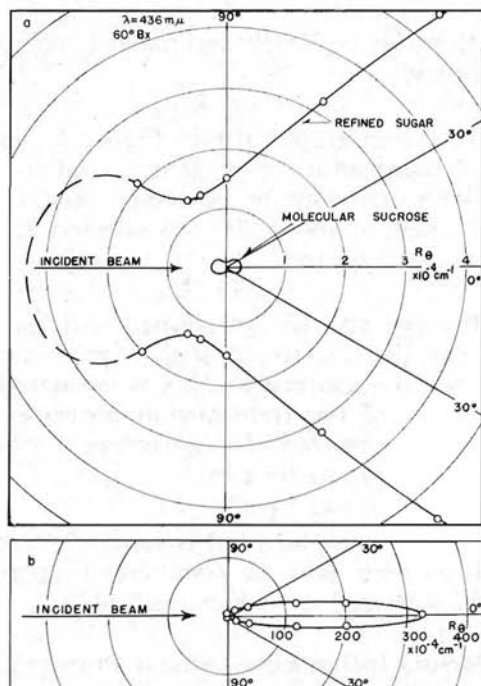


Figure 1.—Scattering envelope of a refined sugar compared with that of molecular sucrose in polar coordinates. In Figure 1b the scale has been decreased 100-fold to show the complete envelope of the refined sugar.

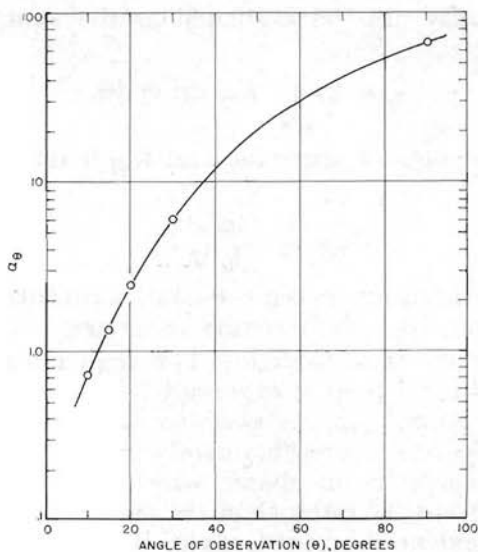


Figure 2.—Dependence of a_{Θ} on angle of observation.

of a sugar solution can be closely estimated from a single scattering of measurement

$$\tau = a_{\Theta} R_{\Theta}$$

Values of a_{Θ} are shown graphically in Figure 2. This appears to be a property of sugar solutions in general and is not a function of any particular instrument or geometry used to measure the scattering. The angle of about 20° was selected as most suitable, in which case $a_{20} = 2.45$ and

$$\tau = 2.45 R_{20}$$

The turbidity can also be determined with equal facility by measuring all the light scattered within an integrating sphere (2). In either case, the scattering index is evaluated by a method that is independent of the transmission measurement, and the attenuation can be "corrected" for scattering to obtain by difference the true absorption as follows:

$$a_s = a^* - s$$

Table 1 gives some examples of this separation of "color" and "turbidity". It is seen that in commercial sugar liquors, the fraction of light scattered is seldom negligible.

Factors Influencing Optical Properties

It is of considerable interest to review some of the various factors that influence the absorbancy and scattering indices of commercial sugar solutions.

Table 1.—Separation of absorption and scattering of sucrose solutions.
 $\lambda = 436 \text{ m}\mu$; concentration = $\sim 35^\circ$ Brix

Type	a^s	s	a ($a^s - s$)	Percent light lost by scattering
	$-\log T$ bc	$\frac{\tau}{2.303c}$		
Granulated:				
Medium	0.0315	0.0238	0.0077	75.5
Medium	.0134	.0066	.0068	49.3
Fine	.0722	.0391	.0331	54.2
Tablets	.0452	.0182	.0270	40.3
Washed	.7072	.428	.2792	60.5
Washed	.6154	.400	.2154	65.0
Soft	22.66	2.16	20.5	9.53
Hawaiian raw	4.04	0.507	3.53	12.5
Cuban raw	5.56	.782	4.78	14.1

Dependence Upon Wave Length

The dependence of optical measurements with wave length for sugar solutions is well known. Attenuation index curves for some typical sugar products over the visible and ultraviolet spectrum are shown in Figure 3. It is noted that all sugars behave in a quite similar manner, showing no maximum. In some cases inflections are found at $280 \text{ m}\mu$.

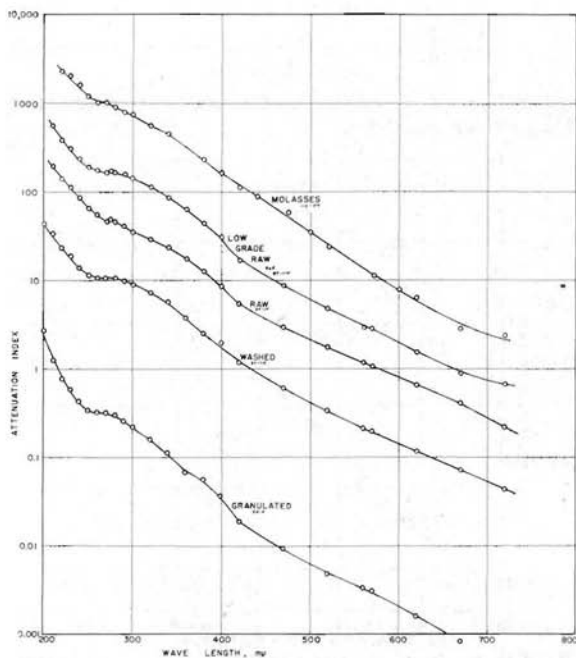


Figure 3.—Attenuation indices for typical sugars.

The dependence of scattering in sugar liquors upon wave length has not been as completely investigated as the other aspects of scattering, but it is safe to say that the effect is not nearly as steep as in the case of absorption. This fact is the basis of the so-called "subtractive" turbidity corrections which will be considered later.

Refractive Index

The effect of refractive index on turbidity is shown in Figure 4. These data were obtained by adding a constant small amount of a raw sugar solution to purified sucrose solutions of different

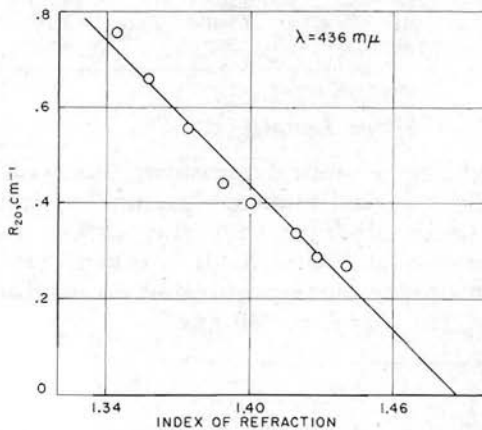


Figure 4.—Effect of refractive index on scattering at constant concentration of scattering particles.

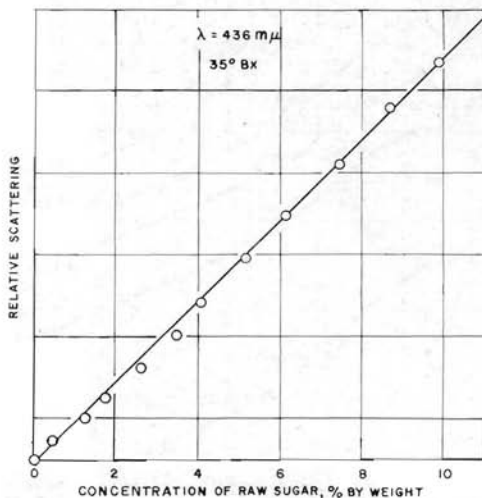


Figure 5.—Effect of concentration of scattering particles at constant refractive index.

densities. As the refractive index of the medium approaches that of the colloidal material causing the scattering, the turbidity approaches zero. For this reason, not all colloiddally dispersed materials scatter light.

At constant refractive index, the turbidity increases directly with the number of scattering particles. This is shown in Figure 5 where the data were obtained by adding known small amounts of a raw sugar solution to a purified sucrose solution. When a commercial sugar is dissolved in water at various concentrations, the effect is the product of these two as shown in Figure 6. At low concentrations the turbidity increases with the concentration of sugar solids and reaches a maximum at about 35° Brix. At higher concentrations there is a decrease in the turbidity due to

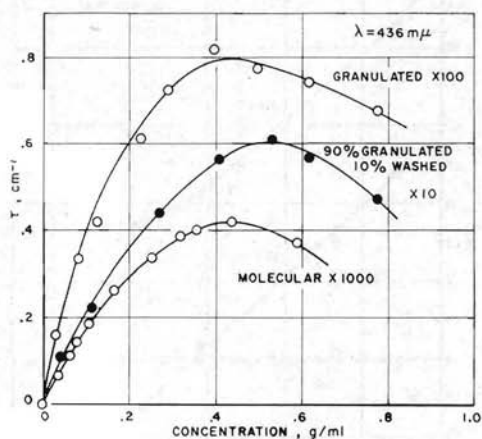


Figure 6.—Effect of sucrose concentration on turbidity.

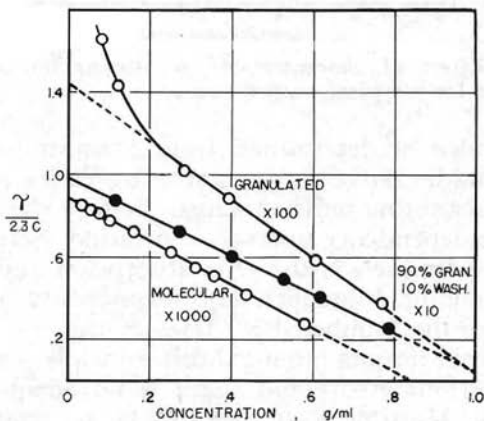


Figure 7.—Effect of sugar concentration on the scattering index.

the increase in refractive index. The same effect is observed for highly purified sucrose, granulated sugar, and for liquors in process. The turbidity may be expressed as a scattering index, which is the more pertinent method of expressing light scattering data because it is additive with absorbancy and attenuancy. The turbidity data of Figure 6 are thus expressed as scattering index in Figure 7. This decreasing behavior with increase of solids concentration is characteristic of light scattering in sugars. It can be traced to the refractive index effect. The attenuation index behaves in similar manner. The upper curve in Figure 8 is the

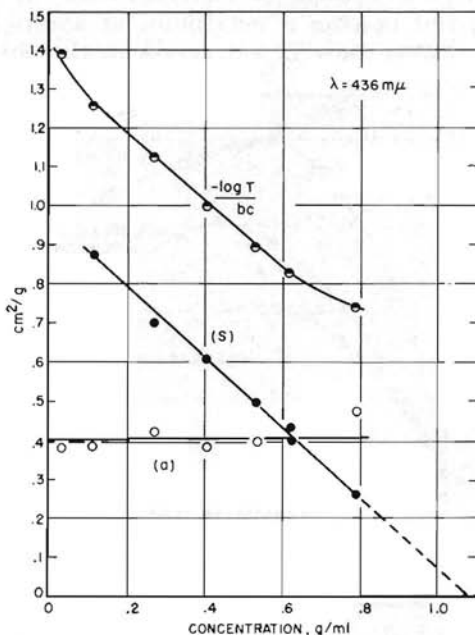


Figure 8.—Effect of concentration on attenuation, absorption, and scattering indices for a typical washed sugar.

attenuation index as determined from a transmission measurement. The middle curve is the scattering index as determined from forward scattering measurements. Both of these curves show the same sharp dependence upon concentration (refractive index). Their difference, which is the true absorption and directly correlates with colorant, is independent of concentration as it should be according to the Lambert-Beer law.

Highly turbid liquors often exhibit multiple scattering. This can lead to serious errors and there is no adequate theory to account for it. Multiple scattering can be recognized by a very high apparent turbidity. It can be avoided by dilution with

extra pure sucrose solution of the standard density. Dilution until the turbidity is less than 0.1/cm will always eliminate it.

Dependence on pH

A very important behavior of the sugar impurity is the dependence of the attenuation index upon pH. The visual appearance of many sugar solutions is strongly dependent upon the pH. The strong variation of a^* at various wave lengths is shown in Figure 9 and this is characterized by a maximum change with pH in the neighborhood of pH = 7. It has been found that the scattering index is almost independent of the pH of the liquors and, hence, the entire effect noted in Figure 9 is due to changes in the absorbancy index. This may be due to changes in molecular form of the impurities. When a determination of the amount of impurity is desired, the pH must be brought always to the same level, since obviously, a change in pH does not change the total amount of impurity.

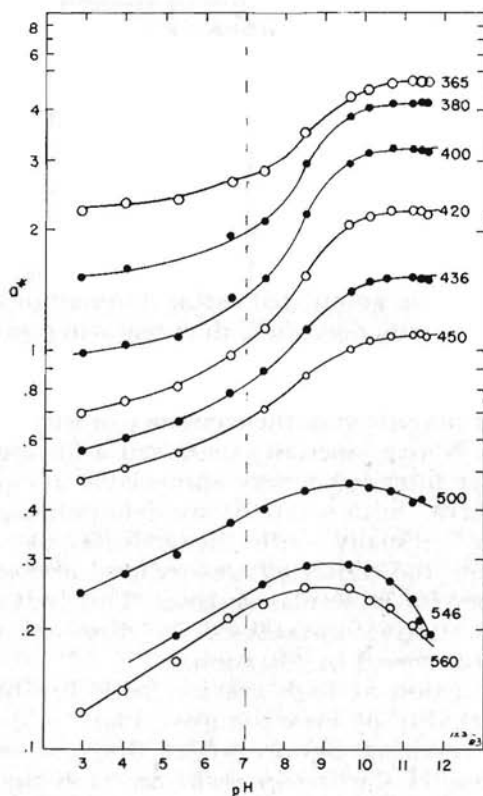


Figure 9.—Dependence of a^* on pH for solution of a washed Cuban raw observed at 38° Brix over a range of wave length.

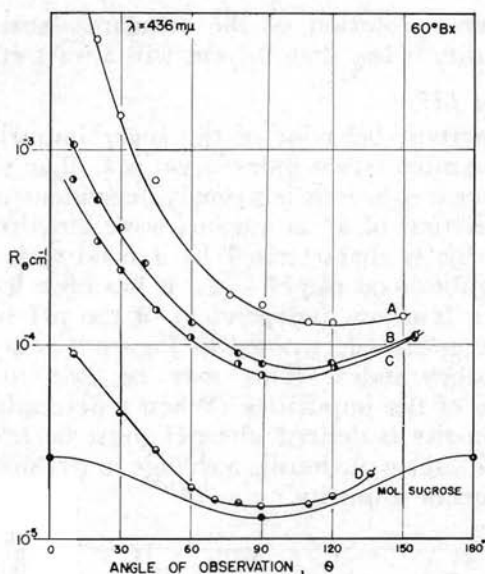


Figure 10.—Angular scattering by solutions of a granulated sugar filtered through various media: A — Coarse sintered glass; B — 0.8 μ Millipore; C — 0.45 μ Millipore; D — Powdered carbon on a 0.45 μ Millipore.

Filtration and Centrifugation

It is important to note at this point, the effect of filtration upon light scattering. Figure 10 shows the angular scattering from solutions of a granulated sugar filtered through various media. As the porosity decreased, thus removing greater fractions of the scattering particles in the filtration, the amount of scattering decreased. The scattering decreased about equally at all angles (further indication of the constancy of shape of the scattering envelope). Notice especially that even a filtration through a 0.45 μ Millipore filter left a very appreciable amount of scattering in the effluent. Such solutions are definitely not to be called "turbidity free." Finally, with the addition of an absorbent, activated carbon, the scattering was reduced almost to that predicted by theory for molecular sucrose. This indicates that part of the light scattering was caused by dissolved material that could never be removed by filtration.

Centrifuge action at high gravity fields has been found to modify the turbidity of sugar liquors. Plots of the attenuation index of the resulting liquors under different conditions are shown in Figure 11 starting in each case with the same Cuban raw. The attenuation index decreased with increase in field and after 150,000 times gravity it was considerably less dependent on

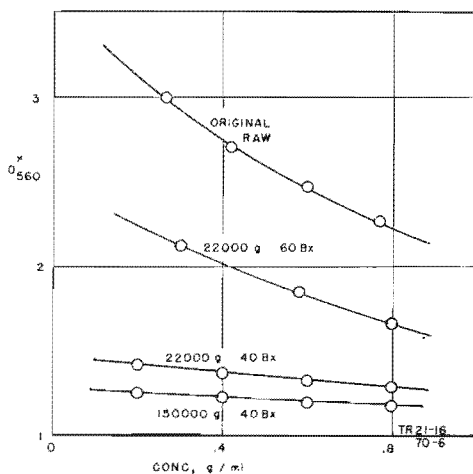


Figure 11.—Factors that influence the centrifuge action on a Cuban raw ($^{\circ}$ Brix, gravity field).

sugar solids concentration which indicates less scattering. A deposit was observed at the top, sides and bottom of the centrifuge tube. Obviously, the colloidal material in the sugar liquor is a mixture of varying degrees of buoyancy. A high speed ultra centrifuge is not a simple means of separating the soluble colorant from the material responsible for the high degree of forward scattering. The most helpful technique is to measure the turbidity.

Fluorescence

One other feature of commercial sugar solutions that must be mentioned in order to complete this discussion is the strong fluorescence in impure sugars. Since the fluorescent light is always at a longer wave length than the exciting wave length, an error in transmittancy or scattering measurements is introduced only when the detector responds to wave lengths longer than the exciting beam. It can be eliminated very simply by inserting a filter in front of the detector. An inexpensive color glass is generally satisfactory because the fluorescent wave length is somewhat removed from the exciting wave length. The use of fluorescence as a measure of impurities in commercial sugar liquors has not been adequately studied.

Instrument Error

Scattering also influences the measurement of sugar color in other ways. As was already mentioned, the attenuation index is the measure of the amount of light removed from the incident beam of both absorption and scattering. However, the scattered

light is mostly scattered forward through only a very small angle and thus emerges from the cell very close to the transmitted beam. If the aperture in front of the photocell is made a little large to avoid the need for careful optical alignment, as is usually the case, then part of this light that was scattered from the beam may be included in the measurement as if it were part of the beam, as illustrated in Figure 12. Thus, the instrument sees less removal of light than was actually the case and an error results in that the indicated attenuation is reported too low.

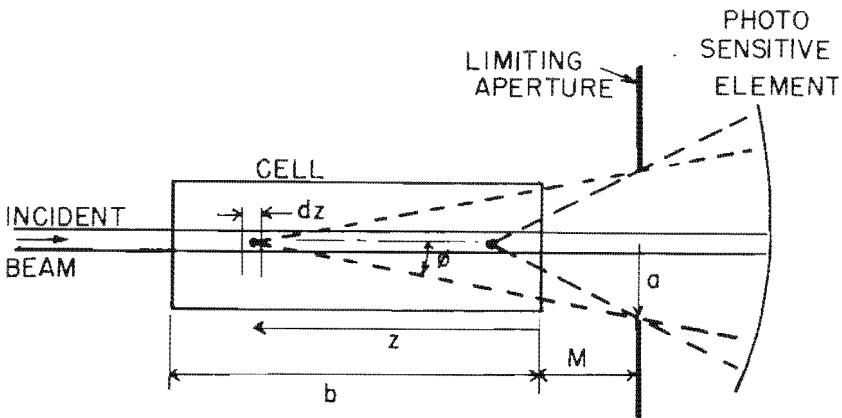


Figure 12.—Geometry of transmission measuring instruments showing how forward scattered light is measured along with transmitted beam: a = radius of limiting aperture; M = distance from exit end of cell to limiting aperture; b = length of cell; z = distance from exit end of cell to scattering particle.

It is essential, therefore, to evaluate the amount of forward-scattered light that is mistakenly measured with the transmitted beam. This error is inherent in all transmission measurements on commercial sugar liquors since these always contain some residual turbidity. It is obvious that the geometry of the instrument used for the transmission measurements is important. The detector element of different instruments can vary as to the limiting aperture with which the scattered light is received. This subject has been carefully studied and is discussed in another publication (14). Errors by as much as a factor of 2 are not uncommon, but all can be reduced by a slight instrument modification.

Choice of Conditions for Color Evaluation

From the foregoing discussion of the factors that influence the optical measurements, it should be evident that the complete optical evaluation of a sugar solution requires the independent evaluation of both attenuation and scattering. The absorbancy

index can then be determined by difference. However, the scattering should be looked upon as more than a mere correction to obtain absorption; it is by itself an additional measure of another class of impurities. Because a suitable light-scattering instrument is not yet available at a reasonable cost, most laboratories will have to rely on the attenuation measurement. It must be appreciated that this measurement always includes light scattering. The conditions of measurement which must be specified are the wave length, pH, and sugar concentration.

Choice of Wave Length

In regard to wave length, a monochromatic source in the blue, violet, or very near ultraviolet undoubtedly has real advantages. One guide in the selection of a particular wave length is the desirability that it correlate somewhat with visual appearance; thus, the measurement is made to serve a dual nature. In the charts for evaluating the E_{NBS} unit (6) of visual appearance, it is readily seen that the value obtained depends more upon the reading at 420 $m\mu$ than the one at 560 $m\mu$. In spite of the fact that the dominant wave length for sugars is about 580 $m\mu$, and that the greatest response of the human eye occurs at 550 $m\mu$, the skewed attenuancy curve for sugars brings the single wave length for best correlation with visual appearance well into the blue. Any wave length in the blue appears to serve quite well, but the higher attenuancy in the extreme blue assists in the precision. This can become a factor for highly refined sugars that exhibit little color. The wave length of 420 $m\mu$ or the mercury lines at 365, 405 or 436 $m\mu$ appear as feasible choices.

The attenuancy increases with decrease in wave length according to an inverse 3rd to 8th power law. Such a steep dependence requires a close specification as to the wave length when reproducibility and precision are desired. It is not adequate to isolate the desired spectral region by means of optical filters. In addition to prism or grating spectrometers, interference filters (transmission type) may be used as a source of monochromatic light. For greater intensities the emission lines of the mercury arc are very useful as a monochromatic source.

Choice of pH

In sugar processing it is essential to keep the pH in the range of acid-base neutrality for the majority of the time. Lower values than pH 7 are avoided because of sucrose inversion and higher values are undesirable because of chemical reactions leading to alkaline degradation at the processing temperatures. However, there are serious disadvantages to the use of pH 7 in the optical evaluation of sugar liquors. It is difficult in a short time to obtain

a precise measure of the pH because of the slow approach to steady state by a pH meter. This is caused mainly by slow diffusion at the salt bridge of the reference electrode in highly viscous media. Moreover, the slope of the a^* versus pH curve at 420 $m\mu$ in the neighborhood of pH = 7.0 is so steep that an error of 0.1 in pH results in an uncertainty in a^* of 5% or more. It is, therefore, highly desirable to use a value where a slight error in pH will produce a minimum change in the absorbancy or attenuation. This occurs obviously in the neighborhood where the curves of Figure 9 have zero slope. At 560 $m\mu$ this is at pH 9 while at 420 $m\mu$ or thereabouts this occurs at pH 10 to 12 and apparently again below pH 3. A high pH gives a greater attenuation to measure, but otherwise any flat portion on the curves of Figure 9 is a good region to use. There may be a chemical instability of the colloidal scattering particles at extreme values of pH that would influence the scattering reading. However, this can be circumvented by making the readings promptly after the pH adjustment is made.

Choice of Concentration

The absorption index can be properly measured at any concentration, but the attenuation index, because of its dependence upon scattering (which is in turn dependent upon the refractive index) is dependent upon the concentration. Any convenient solids concentration is satisfactory, but all measurements should be made at the same concentration. Liquors of 60° Brix and above are most difficult to handle in optical cells due to the need to eliminate striations. Liquors of 50° Brix and below do not present this difficulty. The turbidity is greatest and easiest to measure at 35° Brix, but a greater dilution is to be avoided since this decreases the magnitude of the measurement. All these factors influence the choice of concentration, but once it is selected it should be rigidly adhered to for all measurements. Further dilution of very dark products such as molasses, should be made with extra pure sucrose of the selected concentration instead of water to keep the same refractive index.

A Recommended Procedure

This paper could hardly be considered complete without recommending a procedure that meets the requirements set forth. The conditions of measurement which have been found most suitable are:

Wave length	365 $m\mu$
pH	11 \pm 1
Brix	35 \pm 1

These conditions were chosen to define a unique attenuation index in a procedure that is quick, easy, precise, and a good

measure of the concentration of colorant. The procedure for attenuation index only is as follows:

1. Prepare a solution of the sugar to be tested at 35 ± 1° Brix by diluting with 0.1N NaOH. If the original solution is 60° Brix, dilution with an equal volume falls within the range. Other original densities require slightly different dilutions. This procedure automatically adjusts the pH to 11 ± 1.
2. Place the solution in an absorption cell whose path length was chosen to keep the measurement between 10 and 90% transmission. Further dilution, if required, must be made with a high-quality granulated sugar solution of 35° Brix. A cell depth of 5 cm is adequate for even the lightest colored sugar.
3. Measure the attenuancy at 365 m μ wave length using an instrument which was designed or modified to exclude as much as possible of the forward-scattered light from being measured along with the transmitted beam.
4. Report the results as the attenuation index:

$$a^*_{365-11-35} = (-\log T)/bc$$

When a light-scattering instrument is available, the same conditions are used, and both attenuation and scattering are measured in the same instrument. The procedure is extremely simple once the calibration has been made. The measurement is made at a cell depth required by the instrument and always at the same concentration of 35° Brix, and the same pH of 11 ± 1. Highly turbid liquors require further dilution with a purified sucrose solution of 35° Brix in order to eliminate multiple scattering.

After the instrument is properly adjusted, the cell containing the sugar liquor is placed in the measuring compartment and two readings made, one of the transmitted light G_T and one of the scattered light G_s at a well defined angle. The scattering index is then calculated as:

$$s = k \frac{G_s}{G_T}$$

The constant k is a very complex function of: (A) the concentration of the solution, (B) the refractive index of the solution, (C) the angle of the scattering observation, (D) the width of various beam-defining slits in the instrument, and (E) the optical density of a filter in the transmitted beam. Fortunately, several calibration methods are available and the value of the constant is easily determined (13, 15).

The attenuation index is determined at the same time from the transmission reading and an additional reading for water, $G_{T(\text{water})}$. The transmittancy is then evaluated:

$$T = \frac{G_T}{G_{T(\text{water})}}$$

The attenuation index is calculated in the usual manner and the true absorbancy obtained by difference.

Discussion: Critique of Various Methods for Measuring Sugar Color

In view of the optical properties of sugar solutions, it is of interest to examine those procedures that have already been proposed to measure sugar color in order to see how they comply with the necessary conditions.

Visual Appearance

Visual appearance methods, of which the tristimulus values, Lovibond, F_{NBS} and the method of Brice (4) are examples, are based on a mistaken emphasis and it is the thesis of this paper that visual appearance is not the most important aspect of the problem. Visual appearance is inadequate to deal with commercial sugar solutions. Each method enumerated above was designed for non-turbid solutions and either ignores turbidity, requires a low level of turbidity, or makes a crude "correction" for turbidity. Yet turbidity is definitely a part of visual appearance. Visual appearance methods are sometimes used at a prescribed concentration and cell depth and if the pH were also specified, as is sometimes done, then these methods may produce an approximate measure of amount of impurity. The scattering has not been sufficiently considered and the effective wave length is a peculiar "average" over some of the visible region.

Visual Comparators

The visual comparison methods (8, 19) such as Stammer, Horne, Scott-Klett and G & H, in which the sugar solution is compared with a standard glass or colored solution of inorganic salts, depend on an empirical standard. These should not be confused with visual appearance methods. The eye is used only to detect differences. Very precise results could be obtained, but there is considerable difficulty in reproducing any of these standards. It is almost impossible to reproduce various melts of a colored glass and it is not practical to obtain a good match in hue with actual sugars. Even the chemical solutions of inorganic salts (8, 19) have limited reproducibility and have the added inconvenience of frequent liquid manipulations in filling the

reference cell. Furthermore, a light source having a broad band of wave lengths is used and small differences in the light source, or among individual observers, can produce errors. The methods proposed in the past have not always specified a reference concentration or pH. Also, light scattering was not adequately considered. Each observer tends to "correct" a little more or a little less for the turbidity so the value actually obtained appears to be somewhere between the attenuancy and the absorbancy.

White Light Transmission

Attempts to get a better "average" concentration of impurities, or to obtain a measure of visual appearance, have prompted some workers to use white light. In any broad band colorimetry, the wave length distribution of the source, and response of the detector are all important factors. The problem of duplicating the source and the detector is a greatly added burden on the already complex problem of sugar colors. The interpretation is more difficult because of the unknown "averaging characteristics" over the spectrum range. The appropriate procedure to account for scattering in white light has not been worked out. The use of white light with filters at the detector to approximate the standard observer can be traced to the mistaken emphasis on visual appearance. Fortunately, there is now general agreement by many investigators to use a monochromatic light source.

Monochromatic Light Transmission

Transmission measurements at the wave lengths of 720, 680, 560, 545, 485, 436, 435, 420, 405, and 365 $m\mu$ have been used in various investigations. Only those in the violet (i.e. 485 to 365) meet the desirable conditions proposed above. Failure to specify pH and Brix has sometimes given rather ambiguous measurements but this could be easily corrected in the future. When pH was specified, it was often 7.0 which is not good. The procedure (9) which employs 420 $m\mu$, pH 7, and 50° Brix comes the closest to meeting all the requirements.

Prefiltration

Several attempts (3, 21, 1) have been made to eliminate the turbidity effect by a prefiltration operation. These have not been altogether successful because of the variability in the tightness of the filtration media. However, all such efforts are of only very limited value, because they are based on the false premise that the scattering is caused entirely by suspended particulate matter. Actually, a part of the scattering is caused by dissolved material that filtration can never remove. This is another example of errors that have arisen from false concepts of the optical properties of commercial sugar solutions.

Subtractive Methods

Attempts have been made to use transmission measurements at long wave lengths as a measure of "turbidity". Examples are those of Keane and Brice (10) who used a band defined by a red filter (Corning traffic red, No. 245), and Gillett, Meads and Holven (7) who proposed the wave length of 720 $m\mu$.

Thus, the attenuation in the red (or a constant times this value) subtracted from that in blue was considered to correct the latter reading for turbidity. This method is applicable only if the sugar solution has essentially no absorption in the red, and at the same time be so turbid as to have a large scattering in the red. This description fits only some granulated sugars. The major failing of the method occurs when attempts are made to extend it to sugar liquors containing higher levels of impurities. In general, the attenuation, absorption and scattering indices of different sugars have different wave length dependences. For instance, the wave length exponent of attenuation has been observed to range between 3 and 8. This is indeed a very large change. It is not too surprising, therefore, that these subtractive corrections for turbidity sometimes give paradoxical results, such as negative color.

Concluding Remarks

Three optical properties of sugar liquors are currently used extensively in evaluating sugar liquors: optical rotation as a measure of sucrose concentration, refractive index as a measure of total solids, and spectrophotometric absorption as a measure of a class of impurities. Scattering has too long been considered solely as an interference in the absorption measurement and only recently has it been recognized as an additional independent measure of impurities.

A more complete approach to the color problem has been suggested by Liggett and Deitz (12) who used the Kubelkã (11) theoretical solutions relating the absorption and scattering properties of pigments. Evaluation of both the absorption coefficients and scattering coefficients of both the dissolved and suspended material, would provide a more complete understanding of the nature of the optical phenomena. This would result in four parameters, instead of the two which now make up the attenuation index. Such a complication could hardly be justified in the sugar color application at present.

An example of what might be done is shown in Figure 13. The bottom part of the figure represents a plausible arbitrary distribution of particle sizes ranging from molecular magnitudes for degradation fragments having high absorbancy to the colloidal magnitudes showing large forward scattering. The middle curves

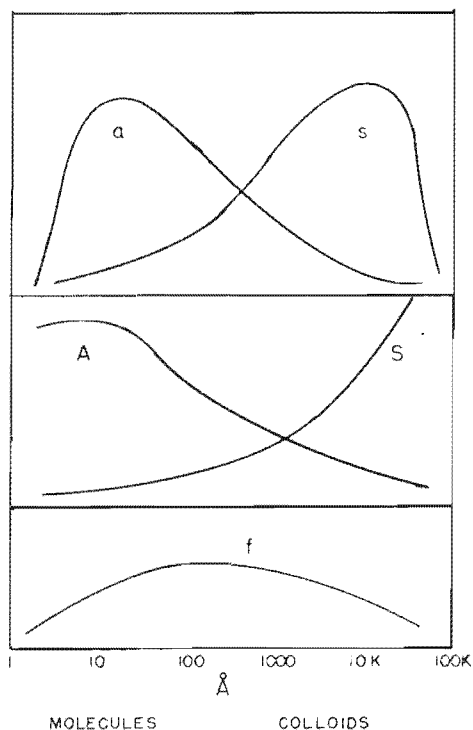


Figure 13.—Simplified dependence on particle size: f = distribution function; A = absorption coefficient; S = scattering coefficient; a = absorbancy index; s = scattering index.

of Figure 13 illustrate possible magnitudes of the absorption and scattering coefficients. The products give the indices in the top curve. The two principal maxima are the justification for the present division of the overall problem into only two parameters, namely the colorant and the scatterer. A more complete evaluation would have to consider the entire curves.

Absorbancy values at particular wave lengths have been proposed by many as a measure of single constituents or small groups of constituents, but, with one exception, the results have been very discouraging. The exception is the detection of HMF (hydroxymethylfurfural) in acid-hydrolysis products (17, 18, 20). Apparently, the attenuation index versus wave length of all the sugar impurities are so nearly the same that there is little hope of distinguishing among them optically. On the other hand, much of the work was done without a sufficient appreciation for scattering, and, if true absorption were properly evaluated, more significant progress might have been made.

An examination of the general shape of the whole spectrophotometric attenuancy curve shows that definite differences or trends can be found among commercial sugars. This observation has been expressed in various ways, one of which is by the wave length exponent (12). In general, more turbid sugars have a lower exponent than the less turbid sugars. But again, many of these observations were made without a satisfactory differentiation between absorption and scattering. Further studies in the light of present day knowledge might well prove fruitful.

Fluorescence is very weak in very highly refined sucrose and strong in raw sugars. This readily-measured optical property most certainly has promise as an additional measure of a class of impurities. Virtually no work has been done in this field with commercial sugar products and a wide open opportunity may await a careful investigator.

The effect of pH on absorbancy has possibilities as another measure of a class of impurities. Some sugars show a greater pH effect than others. A distinction could be made between pH sensitive colorant and pH insensitive colorant by measuring a^* at two different pH's. However, the absolute amount cannot be determined from transmission measurements alone due to the contribution of the scattering index as illustrated in Figure 14.

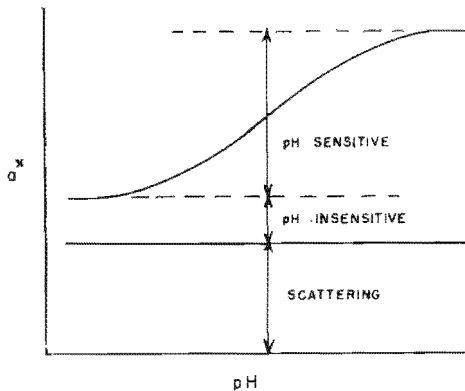


Figure 14.—Three aspects of the dependence of a^* on pH at constant wave length.

Literature Cited

- (1) BERNHARDT, W. O., F. G. EIS, and R. A. MCGINNIS. 1958. Measurement of color and turbidity in solutions of white granulated sugars. Presented at the 134th Meeting of A.C.S., Chicago, Ill., Sept. 7-12.
- (2) BERNHARDT, W. O., F. G. EIS, and R. A. MCGINNIS. 1962. The sphere photometer. *J. Am. Soc. Sugar Beet Technol.* 12 (2): 106-126.

- (3) BREWSTER, J. F., and F. P. PHELPS. 1930. Color in the sugar industry. III. Preparation of asbestos for use as a filter aid. *Ind. Eng. Chem., Anal. Ed.* 2: 373.
 - (4) BRICE, B. A. 1960. Glass color standards and a uniform chromaticity scale for sugar products. *J. Opt. Soc. Amer.* 50: 49-56.
 - (5) DEITZ, V. R., N. I. PENNINGTON, and H. L. HOFFMAN, JR. 1952. Transmittancy of commercial sugar liquors: Dependence on concentration of total solids. *J. Research NBS.* 49: 365-369. RP2373.
 - (6) DEITZ, V. R. 1956. Color evaluation in the cane sugar industry. *J. Research NBS.* 57: 159-170. RP2706.
 - (7) GILLETT, T. R., P. F. MEADS, and A. L. HOLVEN. 1949. Measuring color and turbidity of white sugar solutions. Development of photoelectric method and apparatus. *Anal. Chem.* 21: 1228-1233.
 - (8) GILLETT, T. R. 1953. Color and colored non-sugars. Principles of Sugar Technology. Vol. 1, Chap. 8: 214-290. P. Honig, editor, Elsevier Publishing Co., New York.
 - (9) INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS. 1958. Color and turbidity of sugar products and the reflectancy of solid sugars. Subject 13: 51-58.
 - (10) KEANE, J. C., and B. A. BRICE. 1937. Photoelectric grading of white sugars and their solutions by reflectance and transmittancy measurements. *Ind. Eng. Chem., Anal. Ed.* 9: 258-263.
 - (11) KUBELKA, P. 1948. New contributions to the optics of intensely light-scattering materials. Part I. *J. Opt. Soc. Amer.* 38: 448-457.
 - (12) LIGGETT, R. W., and V. R. DEITZ. 1954. Color and turbidity of sugar products. *Advances Carbohydrate Chem.* 9: 247.
 - (13) MARON, S., and R. LOU. 1954. Calibration of light-scattering photometers with ludox. *J. Polymer Sci.* 14: 29.
 - (14) NATIONAL BUREAU OF STANDARDS. 1960. Bone Char Research Project, Inc. Technical Report No. 59. Washington, D. C.
 - (15) OSTER, G. 1953. Universal high-sensitivity photometer. *Anal. Chem.* 25: 1165-1169.
 - (16) RIEGER, C. J., and F. G. CARPENTER. 1959. Light scattering by commercial sugar solutions. *J. Research NBS.* 63A: 205-211.
 - (17) SCALLET, B. L., and H. J. GARNER. 1945. Formation of 5-hydroxymethylfurfural from D-glucose in aqueous solution. *J. Am. Chem. Soc.* 67: 1934-1935.
 - (18) SINGH, B., G. R. DEAN, and S. M. CANTOR. 1948. Role of 5-(hydroxymethyl) furfural in the discoloration of sugar solutions. *J. Am. Chem. Soc.* 70: 517-522.
 - (19) SPENCER, G. L., and G. P. MEADE. 1945. Cane Sugar Handbook. 8th edition: 476-491. John Wiley and Sons, New York.
 - (20) WOLFROM, M. L., R. D. SCHULTZ, and L. F. CAVALIERI. 1948. Chemical interactions of amino compounds and sugars. III. The conversion of D-glucose to 5-(hydroxymethyl)-2-furaldehyde. *J. Am. Chem. Soc.* 70: 514-517.
 - (21) ZERBAN, F. W. 1952. Report on transmittancy of sugar solutions. *J. Assoc. Off. Agr. Chem.* 35: 636-647.
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