Determination of Color of Water and Wastewater By Means of ADMI Color Values

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INTRODUCTION

The American Dye Manufacturers Institute (ADMI) is made up of 23 member companies and includes all of the major dyes manufacturing companies. In 1970, ADMI established an Ecology Committee to undertake studies of the effect of dyes on the environment. Such studies were undertaken at several leading universities. As an outgrowth of these studies the Ecology Committee became aware of the need for a more reliable method for the measurement of color of water and undertook the work of devising a method that would meet four criteria.

1. Applicable to any hue.
2. Sensitive to small color differences.
3. Related to APHA values.
4. Require relatively inexpensive instrumentation.

This assignment was well matched to the capabilities of the committee which was made up of some of the most knowledgeable individuals with respect to color theory and measurement in the United States dye industry. The ADMI color value which resulted from this study will be described.

Several methods for obtaining a measurement of the color of water were considered and rejected because of theoretical or practical limitations. These included Complementary Tristimulus Colorimetry (1,2,3,4,5,6,7,8,9,10), Sum of Absorbances at Selected Wavelengths (11) and other unpublished methods. It was considered important that the method devised by related to visual perceptibility rather than to concentration since it is rare that the identity of the colorants responsible for the color of water are known. It is even less common that a single colorant is responsible. Furthermore, it was the judgment of the committee that dyes pose a problem to the environment only in terms of an esthetic effect. A

stream may be considered to be objectionable if it is obviously blue rather than its normal muddy brown color or if it is red rather than a normal blue or green.

The C.I.E. system of specifying color based on the Tristimulus Values X, Y, Z and the trichromatic coefficients x and y derived from the tristimulus values has had wide acceptance in relating physical measurements and the stimuli perceived by the normal observer. Section 206A of the 13th Edition uses this system to specify the color of wastewater in terms of dominant wavelength (hue), purity and luminosity using the familiar chromaticity diagram shown in Figure 1.

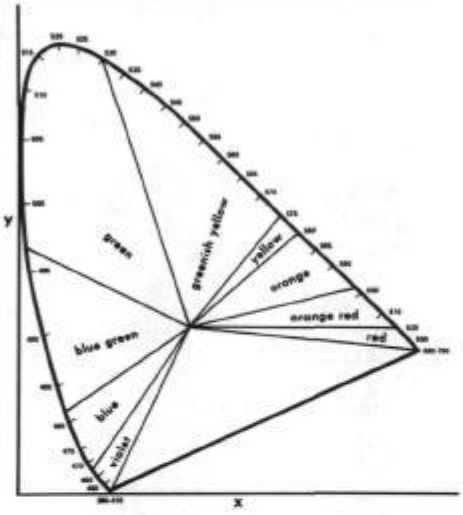

Figure 1 — C.I.E. chromaticity diagram.

MacAdams (12) in 1943 showed that the C.I.E. chromaticity coordinates for colors having slight hue differences but equal visual perceptible difference from a standard did not have equal vectors from the standard (fall on a circle around the standard) but rather fell on an elliptical locus, and even more importantly, the size of these ellipses for an equal visual perceptible difference varied widely depending on the position in the chromaticity diagram as shown in Figure 2.

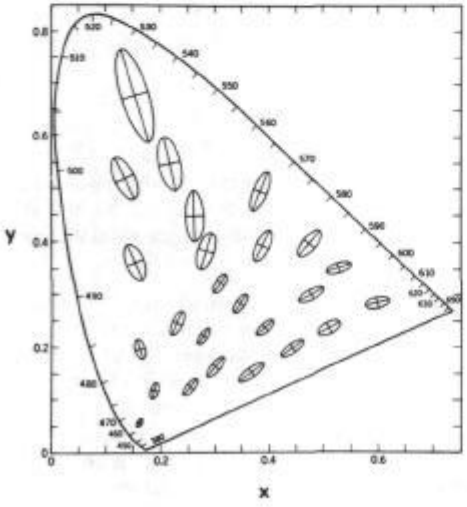

Figure 2 — MacAdam ellipses of equal visual perception in C.I.E. chromaticity diagram.

Many equations have been proposed for calculating "uniform *chromaticity* differences," the object of these equations in effect being to so transform the C.I.E. chromaticity diagram that these different sized ellipses become circles of uniform diameter as shown in Figure 3. The "Uniform *Color* Difference" equations introduce the other dimension of color space (lightness or luminosity) and are extensions of the uniform chromaticity equation so that, in the transformed three-dimensional space, colors which have equal visual perceptible differences from a standard will fall on the surface of a sphere, the radii of these spheres being of equal size regardless of the position of the standard in the color space.

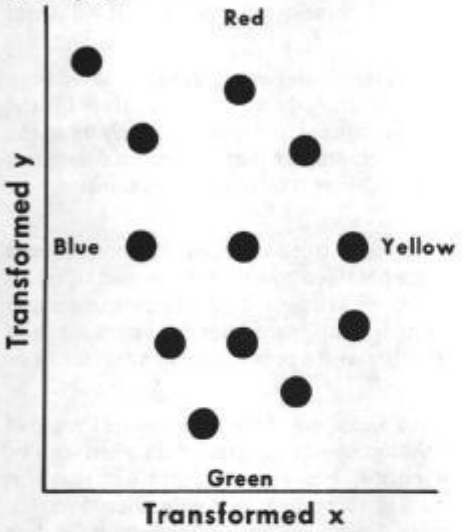

Figure 3 — Transformed ellipses in C.I.E. chromaticity diagram.

The preceding is a gross oversimplification of the very complex problem which color scientists studied for many years. It is intended only as an illustration of the basic concepts of uniform color difference which are the heart of the proposed method.

Many of the "Uniform Color Difference" equations that have been proposed are very complex and require lengthy calculations once the C.I.E. tristimulus values are available. One of the simpler equations to use is that known as the Adams-Nickerson equation combining the "Chromatic Value" transformation of the C.I.E. chromaticity diagram proposed by Adams with the lightness or luminosity modification proposed by Nickerson. A good description of this equation together with very convenient tables for application of the equation is given by McLaren.

In the Adams-Nickerson color difference formula the multiplier 40 or 42 is normally used so that a perceptible color difference is equal to ΔE. It was our feeling that a solution which differs visually, regardless of hue, from colorless to the same degree that the yellow APHA 100 standard differs visually from colorless should also have a value of 100. By measurement of the platinum-cobalt solutions and calculation of ΔE by the Adams-Nickerson formula it was found that a multiplier of about 1,400 was necessary to yield a color difference value numerically equal to the APHA value. The multiplier will vary somewhat from instrument to instrument. A calibration curve based on measurement of platinum-cobalt APHA standards is recommended to obtain accurate ADMI values to describe the color of water when a variety of hues has to be measured.

METHOD FOR DETERMINING ADMI VALUES OF WATER

The ADMI method has been deliberately restricted to become essentially an extension of the color methods described in Section 206 of the 13th Edition of *Standard Methods* (14).

An important consequence of this restriction is that color is defined as what may be termed soluble color; ie, prior to examination all samples are filtered. The clarification procedure specified in *Standard Methods*, namely filtration through a Celite precoat on micrometallic filter crucibles, we find requires somewhat more attention in order to produce sparkling clear filtrate than we believe is necessary. In our hands, the use of a Celite precoat on glass fiber filter paper supported in a Buchner funnel gave very satisfactory results with little attention. This is particularly true where the use of rectangular 5-cm cells may require the preparation of 100 ml or more of filtrate. The Celite treatment will remove some dye from solution by adsorption when *synthetic* solutions of some dyestuffs are so treated; however, limited evidence indicates that this is not the case with some dye-bearing actual industrial wastes which were examined.

The basic procedural step is to generate for the filtered sample by examination either in a spectrophotometer, or a suitable tristimulus colorimeter, the tristimulus values for the sample. Whether this is a simple step or a time-consuming step depends entirely upon the instrumentation which is available. It is important to emphasize that the required data can be obtained with any spectrophotometer which can measure transmittance of solutions in a cell of known path length.

Once the tristimulus values for the sample and for distilled water have been measured or calculated, the corresponding Munsell values are obtained by reference to a set of tables relating such values to the tristimulus values. From the Munsell values for the sample and for distilled water, calculation of the ADMI value is simply accomplished by a series of arithmetical operations which can be carried out either with a pencil, paper and slide rule or a desk calculator.

Methods 206A and 206B in the 13th Edition of *Standard Methods* delineate the use of a spectrophotometer or the old Fisher Electrophotometer to generate data which can be used to determine dominant wavelength and purity. We wish to point out that this procedure also specifies the use of a 1-cm cell path. Except for very highly colored wastes, the procedure we are proposing specifies the use of a 5-cm cell path; therefore, if the data generated by our method are used to calculate the dominant wavelength and purity the values so calculated will be somewhat different from those that would be calculated using a 1-cm cell path.

In this same connection the calculations given in the method in Section 206B do not lead to the correct values for the tristimulus values X, Y, and Z but to values that are intended only as intermediate values to be used in calculating the trichromatic coefficients x and y which are then used to determine dominant wavelength and purity graphically. In fact if the same sample were used in both Methods 206A and 206B drastically different tristimulus values would be obtained.

It is important, of course, to recognize that the method depends upon the assumption that the Adams-Nickerson transformation of C.I.E. color space leads to values which are visually equivalent. It can be readily understood that this assumption becomes less important the closer the hue of the sample is to the hue of the platinum-cobalt APHA standards. However, anyone who has ever attempted to evaluate the intensity of a blue solution with respect to a yellow solution as would be required in the visual APHA method will probably agree that even if the Adams-Nickerson color space is not exactly visually uniform, any nonuniformity will undoubtedly introduce a smaller error than an attempt to arrive at an APHA value by visual means.

If we accept the assumption that the Adams-Nickerson color space is visually uniform, it must be recognized that this transformation in order to be visually uniform depends upon having reasonably accurate tristimulus values for the sample. However, it also can be seen that even this requirement becomes less important when we are dealing with very light colors, particularly those involving ADMI values of 100 or less.

The method requires generating C.I.E. tristimulus values for each sample. If desired,

these can also be used to derive dominant wavelength, purity, and luminance values as described in Section 206A of Sandard Methods.

The method can be divided into five parts:

1. Measurement of Sample on Suitable Instrument.
2. Calculation of C.I.E. Tristimulus Values X, Y, Z (may be inherent in 1).
3. Conversion of X, Y, Z to V_X, V_y, V_Z (from published tables).
4. Calculation of Adams-Nickerson Color Difference (DE).
5. Conversion of DE to ADMI Value.

A few comments regarding these five steps in the method for determining ADMI values are offered to help provide a basic understanding of this new method.

1. A wide variety of color measuring instruments can be employed ranging from complex double-beam ratio recording spectrophotometers coupled to a digital computer or a tristimulus integrator (Diano-Hardy spectrophotometers) through manual, single beam spectrophotometers (Beckman DU) and abridged spectrophotometers (Color Eye) to simple, filter colorimeters. It is important, however, that the instrument be calibrated as described in the Appendix to be published as part of this paper in the proceedings of the conference. The calibration data for one instrument should not be applied to another instrument, particularly a different type instrument or an instrument employing a different cell path length.

2. Some of the more sophisticated spectrophotometers provide tristimulus values directly and thus eliminate much of the calculation time required when transmission values are generated. Depending on the volume of color measurement work to be done and on the precision required, a choice of instruments can be made on economic grounds. When only a few determinations are required per day it may be preferable to use a relatively inexpensive instrument and a desk calculator to obtain ADMI values. At the other extreme a double beam recording spectrophotometer coupled to a digital computer will eliminate calculation time and generate ADMI values within a matter of seconds.

3. Conversion of tristimulus values to Munsell values Vx, Vy and Vz is conveniently accomplished by use of published tables. These tables were produced by using equations by K. McLaren (13).

4. The value DE is calculated from the following equation:

$$DE = \left[(0.23\Delta V_y)^2 + (\Delta(V_X - V_y))^2 + (0.4\Delta(V_y - V_Z))^2\right]^{1/2}$$

where

V_y is the Munsell value equivalent to Y
V_X is the Munsell value equivalent to X
V_Z is the Munsell value equivalent to Z

5. Calculate the ADMI values from a calibration plot of DE versus ADMI value. See Figure 4 a typical calibration curve.

EXPERIMENTAL

Three types of samples were used during this study; APHA standards, solutions of commercial dyes and wastewater samples. The APHA standards were measured during instrument calibration at seven locations in order to estimate between-laboratory reproducibility. Solutions of 45 commercial dyes were evaluated to relate dye concentration to ADMI units. The dyes were selected to represent different end uses and chemical classes. Concentrations equivalent to 50 ADMI units varied from 16.5 to 0.1 mg/l depending upon the inherent tinctorial strength of the dye involved. Wastewater samples were also measured to gain experience at the color levels actually involved at treatment facilities and to compare ADMI values with APHA values determined visually.

A limited number of comparisons between the APHA and ADMI methods made with wastewater revealed significant differences as anticipated. Since no value could be seen in

gathering data to prove that it is difficult if not impossible to visually compare samples of different hue to APHA standards this aspect of the study was not pursued. However, to gain further conficence in the inherent limitation of the APHA method the Committee attempted to judge a blue solution prepared at ADMI 100 with a yellow and a red solution prepared to be significantly less than and more than 100 ADMI, respectively. Only two of the seven individuals who made the visual judgements were able to place the three solutions in their proper order with respect to depth of color.

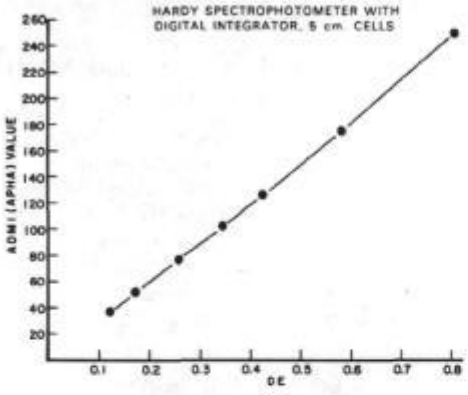

Figure 4 — Calibration curve for Hardy spectrophotometer.

Red, yellow and blue solutions of equal (100) ADMI value do appear to be of the same depth of color. Although this is best demonstrated by actual examination of such prepared solutions in the laboratory, we have prepared a slide to illustrate the point. Photography and color rendition complicate this demonstration but the result is reasonably accurate and illustrates the validity of the method.

PRECISION

Future regulatory requirements will determine the need for precise measurement of color. However, we believe that ADMI color value overcomes a major source of difficulty stemming from variation in hue. The precision attainable is a function of the quality of instrumentation utilized. If small differences in color must be defined, then the instrumentation would become expensive. On the other hand, if future standards permit determination of color within reasonable broad tolerances, then less expensive equipment will be adequate.

Interlaboratory analyses of APHA standards for instrument calibration were performed at seven locations and the results at three APHA levels are shown in Table II. All measurements were made on General Electric recording spectrophotometers. These instruments are widely used for precise work in the dyestuff industry and were readily available to the committee.

A statistical program was used that considers each APHA level individually and computes 95 percent confidence limits for each standard based on the pooled variance calculated for the three standards. Treating the data in this way takes out the established bias from standard to standard and thus estimates only the between-laboratory variability. The F_n value for a single standard obtained in one run in one laboratory has a between-laboratory variability (95 percent C.L.) of ± 68.5. Using the mean F_n determined at APHA 100 this value is equivalent tc about ± 4.9 APHA units. Similar values calculated for the means from seven laboratories are ± 25.9, or ± 1.8 APHA units. Although calibration data for one instrument should not be applied to another, these data indicate the degree of correspondence that can be obtained between different instruments of the same make.

The evaluation of within-laboratory repeatability was based on replicate examination

of dye solutions having ADMI values in the 40 to 150 range. The within-laboratory repeatability was found to be expressed by a 95 percent confidence limit for a single value of ± 0.8 ADMI unit. It is considered highly likely that adequate precision can be obtained with much less expensive and readily available instruments.

CONCLUSION

The ADMI color value provides a measure of the color of water which is independent of hue and thus opens the way to the more accurate definition of the color of water and wastewater. The method has been described to United States Environmental Protection Agency personnel and other interested technical associations who have expressed interest in evaluation of the method.

ACKNOWLEDGEMENT

This work was undertaken by the American Dye Manufacturers Institute (ADMI) through its Ecology Analytical Subcommittee.

APPENDIX

PROCEDURE FOR DETERMINING ADMI COLOR VALUE

Principle

The color of a sample is considered to be the color of the light transmitted by the solution after removing the suspended material, including the pseudo-colloidal particles. It is recognized that the color characteristics of some samples are affected by the light reflection from the suspended material present. However, until a suitable method is available for making solution reflectance determinations, the color measurements will be limited to the characteristics of light transmitted by clarified samples. Suspended materials are removed by filtration through a standard filter aid medium.

This method is based on the premise that the Adams-Nickerson Chromatic Value formula for calculating single number color difference values from C.I.E. tristimulus values adequately transforms C.I.E. color space into a visually uniform color space so that if two colors, A and B, are visually judged to differ from colorless to the same degree, the vector in the transformed color space from colorless to color A will be the same length as the vector from colorless to color B, the length of these vectors being the single number uniform color difference.

Thus a blue solution which would be visually judged to differ from colorless to the same degree that the APHA 100 platinum-cobalt color standard (yellow) differs from colorless would have a vector in Adams-Nickerson Chromatic Value color space from colorless to the point for the blue solution which is equal in length to the vector from colorless to the point for the APHA 100 platinum-cobalt standard, and thus the two colored solutions would have similar single number color difference values. The scaling coefficient has been defined so that the values so calculated are of the same magnitide as the values assigned to the APHA platinum-cobalt standards, that is the ADMI Value for the blue solution would be 100.

Pretreatment of Samples

1. *Apparatus*

The procedure given is taken from 13th Edition of Standard Methods. However, it is considered to be inconvenient and requires attention to produce a clear filtrate. A more convenient procedure is to use the precoat technique on a circle of glass-fiber filter paper (5.5 cm Reeve Angel Glass Fiber Filter Paper Grade 934AH) supported on a Buchner funnel. A filtration system, consisting of the following (see Figure 30, Section 206A (2) of Standard Methods):

a. Filtration flasks, 250-ml, with side tubes.

b. Walter crucible holder.
c. Micrometallic filter crucible, average pore size 40 microns.
d. Calcined filter aid.*
e. Vacuum system.

*Celite No. 505 (Johns-Manville Corporation) or equivalent.

2. *Procedure*

Preparation of sample: Bring two 100 ml samples to room temperature. Use one sample at the original pH value (record pH value), adjust the pH value of the other to 7.6 by using conc. H_2SO_4 or NaOH as required. A standard pH is necessary because of the variation of color with pH. Remove excessive quantities of suspended materials by centrifuging. Treat each sample separately, as follows: Thoroughly mix 0.1 g filter aid in a 10-ml portion of centrifuged sample and filter the slurry to form a precoat in the filter crucible. Direct the filtrate to the waste flask as indicated in Figure 30 (Section 206A (2) of *Standard Methods).* Mix 80 mg filter aid in a 80-ml portion of the centrifuged sample. While the vacuum is still in effect, filter through the precoat and pass the filtrate to the waste flask until clear; then direct the clear filtrate flow to the clean flask by means of the three-way stopcock and collect 70 ml for the transmittance determination.

Spectrophotometry

1. *Apparatus*

a. General

Procedures are given for a wide variety of color measuring instruments. As already pointed out, it is important, however, that the instrument be calibrated as described in Section V and the Calibration data for one instrument not be applied to another instrument, particularly a different type instrument or an instrument employing a different cell path length.

b. Cells

Clean, matched cells with a cell path of 5.0 are recommended where color values are less than 250. Cell paths of 1.0 cm should be used where samples have higher color values; however, calibration must be carried out using appropriate higher APHA platinum-cobalt color standards. When a spectrophotometer is used for color measurement, alternatively samples may be diluted prior to measurement in a 5.0 cm cell and the calculated value multiplied by the dilution factor. This alternative is not recommended when the instrument is a filter colorimeter. In this case a shorter cell path and the appropriate calibration should be employed.

c. Reference Liquid

In all cases the reference is a cell of the same nominal path length filled with distilled water. For all double beam instruments a "100 % line" is measured (both cells filled with distilled water) and these measurements used to generate the X_C, Y_C and Z_C (tristimulus values for "colorless") used in subsequent calculations.

For single-beam instruments, the reference cell is used to set "100 % T" prior to each measurement of the colored solution. In this instance fixed values for X_C, Y_C, and Z given in Section III are used.

2. *Measurement Procedure*

a. Double-beam spectrophotometers equipped with a tristimulus integrator or digital computer giving tristimulus value read-out: Record a "100 % line" (both cells filled with distilled water' from 400 nm to 700 nm with control parameters set so that the read-out will be the values for X,Y,Z (as percentage) for C.I.E. Source C. Designate those values as X_C, Y_C, Z_C. Rinse the sample cell twice and then fill with clarified sample (Section II above) and record the absorption spectrum of the sample in the same manner. Designate the tristimulus values of the sample as X_S, Y_S, Z_S.

b. Double-beam ratio-recording spectrophotometers — Record a "100 % line" (both cells filled with distilled water) from 400 nm to 700 nm with the instrument controls set to

record percent transmittance. Rinse the sample cell twice and then fill it with clarified sample (Section II above) and record the spectrum of the sample in the same manner.

The plotted curves are used to calculate C.I.E. tristimulus values using either the Weighted Ordinate Method, the Ten Selected Ordinates Method or the Thirty Selected Ordinates Method. The tristimulus values for the "100 % line" are designated X_C, Y_C, Z_C, the values for the sample X_S, Y_S, Z_S.

c. *Abridged Spectrophotometers (Color-Eye)*

(1) Using the Four Tristimulus Filters — Follow the manufacturer's instructions for transmittance measurements and calculation of the C.I.E. Tristimulus Values. Use a cell filled with distilled water to generate the tristimulus values for "colorless"" and designate these values X_C, Y_C, Z_C. Use the same cell filled with clarified sample (Section II above) to generate the sample tristimulus values and designate these X_S, Y_S, Z_S.

(2) Using Wavelength Isolation Interference Filters — Follow the manufacturer's instructions for transmittance measurements and calculation of C.I.E. Tristimulus Values (Source C).

Use a cell filled with distilled water to generate the transmittance data for "colorless" and from the values calculate the tristimulus values (Source C) designated X_C, Y_C, Z_C. Use the same cell filled with clarified sample solution (Section II above) to generate the "sample" transmittance data and from these data calculate the tristimulus values (Source C) designated X_S, Y_S, Z_S.

d. Single Beam Manual Spectrophotometers (Beckman DU-2) — fill the reference cell with distilled water and fill the matched sample cell with clarified sample. At each required wavelength, set the transmittance scale to 100 percent. With the reference cell in the light beam balance the instrument as detailed in the manufacturer's instructions, then move the sample cell into the light beam, bring the instrument to balance by adjusting the transmittance knob, then read and record the percent transmittance at that wavelength. Replace the reference cell in the light beam, adjust the wavelength scale to the next required wavelength and repeat.

The wavelengths at which transmittance measurements must be made depend on which method of Calculating C.I.E. Tristimulus Values is employed, the Weighted Ordinate Method, the Ten Selected Ordinates Method or the Thirty Selected Ordinates Method. Convenient work sheets for calculation of the tristimulus values X_S, Y_S, Z are given. In this instance only the tristimulus values for "colorless" are fixed as follows:

$$X_C = 98.06$$
$$Y_C = 100.00$$
$$Z_C = 118.14$$

Conversion of C.I.E. Tristimulus Values to Munsell Values and Calculation of ADMI Color Value.

1. Convert the six C.I.E. tristimulus values X_C, Y_C, Z_C and X_S, Y_S, Z_S to the corresponding values for V_X, V_Y, and V_Z by the use of tables giving the interdependence of X and V_X, Y and V_Y, Z and V_Z (the most convenient tables are in *J. Soc. Dyers and Colorists*, 86, No. 8, 354 (1970); Tables 6.4 (A), 6.4 (B), and 6.4 (C) of *Color Science* (15) by Wyszecki and Stiles, Wiley, N.Y., 1967: or Tables A, B, and C in the Appendix of *Color in Business, Science and Industry* (16), 2nd Edition, by Judd and Wyszecki, Wiley, N.Y. (1963).

2. Calculate the intermediate value DE from the following equation:

$$DE = \left[(0.23\Delta V_y)^2 + (\Delta(V_X - V_y))^2 + (0.4\Delta(V_y - V_Z))^2\right]^{1/2}$$

A work sheet convenient for carrying out the tabulation and calculations required is given.

3. Calculate the ADMI value by interpolation on a plot of DE versus ADMI value or

by one of the other alternatives given in Section V-3.

V. *Calibration of Color Measuring Instrument*

1. *Preparation of Standards*

a. Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6 (equivalent to 500 mg metallic platinum) and 1.00 g crystallized cobaltous chloride, $CoCl_2 \cdot 6H_2O$ (equivalent to about 250 mg metallic cobalt) in distilled water with 100 ml conc. HCl and dilute to 1,000 ml with distilled water. This stock standard has a color of 500 units.

b. If potassium chloroplatinate is not available, dissolve 500 mg pure metallic platinum in aqua regia with the aid of heat; remove nitric acid by repeated evaporation with fresh portions of conc HCl. Dissolve this product, together with 1.00 g crystallized cobaltous chloride, as directed above.

c. Prepare standards having colors of 25, 50, 100, 150, 200 and 250 by diluting 5.0, 10.0, 20.0, 30.0, 40.0, and 50.0 ml stock color standard with distilled water to 100 ml in volumetric flasks. Protect these standards against evaporation and contamination.

2. *Spectrophotometry of Standards*

a. Carry each standard through the spectrophotometry procedure appropriate for that instrument being used as described in Section III above.

b. Calculate for each color standard values for X_S, Y_S, Z_S. If the spectrophotometry was all carried out at the same time a single "100 % line" recording will suffice to generate values for X_C, Y_C, Z_C.

3. *Calculation of Calibration Factor (F)*

a. From the values of X_S, Y_S, and Z_S for each color standard and the values for X_C, Y_C, and Z_C, calculate for each color standard the intermediate value DE as described in Section IV above.

A plot of $(DE)_n$ on the X axis and ADMI value on the Y axis should be prepared. Then when a sample is carried through the procedure and the intermediate value DE has been calculated, this plot can be used to determine the ADMI value. Figure 4 illustrates such a plot for one recording spectrophotometer equipped with a tristimulus integrator.

b. As an alternative to the use of a calibration graph as described in a. above, an empirical equation relating DE and ADMI (APHA) value may be developed. The data from the spectrophotometers have been found to give a good fit to a hyperbolic equation of the form:

$$\text{ADMI Value} = \frac{DE}{a + (b \times DE)}$$

The "least squares" evaluation of the coefficients a and b is described in "Precision Measurement and Calibration," Vol. 1, *Statistical Concepts and Procedures*, SP300, National Bureau of Standards, p. 234. For one recording spectrophotometer a was 3.503×10^{-3} and b was -2.689×10^{-4}.

c. Calculate for each color standard the calibration factor $(F)_n$ by the following equation:

$$(F)_n = \frac{(APHA)_n\,(b)}{(DE)_n}$$

where $(APHA)_n$ = APHA Color Value for Standard n.

$(DE)_n$ = Intermediate value calculated as above for Standard n.

b = Cell path used in spectrophotometry, cm.

For undemanding work the values for (F)n may be averaged to give a mean value of F to use in the calculation of ADMI values of samples as shown in Step 8 of the work sheet (Table I).

F should be approximately 1.4×10^3 for the mean of APHA 50, APHA 100, and APHA 150 standards as measured on a recording spectrophotometer equipped with a tristimulus integrator (Table II).

Then $$\text{ADMI Value} = \frac{(F)\,(DE)}{b}$$

Calculation of the C.I.E. tristimulus values is described and illustrated and a work sheet for calculation of ADMI values from Munsell values is also included. Alternatively, tristimulus values may be calculated by the 10 or 30 selected ordinate methods as described in Section 206A of the 13th Edition of *Standard Methods for the Examination of Water and Waste Water Treatment* (14).

TABLE I
WORK SHEET FOR CALCULATION OF ADMI VALUES FROM C.I.E. TRISTIMULUS VALUES

C.I.E. Tristimulus Values	V_x	V_y	V_z	$(V_x - V_y)$	$(V_y - V_z)$	
X_c =						
Y_c =						
Z_c =						
X_s =						
Y_s =						
Z_s =						
Step (1)	ΔV_y =					
Step (2)	$0.23\Delta V_y$ =				$(0.23\Delta V_y)^2$ =	
Step (3)			$\Delta(V_x - V_y)$ =		$(\Delta(V_x - V_y))^2$ =	
Step (4)				$\Delta(V_y - V_z)$ =		
Step (5)				$0.4\Delta(V_y - V_z)$ =	$(0.4\Delta(V_y - V_z))^2$ =	
Step (6)					Sum =	
Step (7)	DE = $\sqrt{\text{Sum}}$ = $\sqrt{\quad}$ =					
	Calibration Factor (F) =					
	Cell Path Length, cm (b) =					
Step (8)	ADMI Value = $F \frac{DE}{b}$ = ( ) x ( )					

CALCULATION OF C.I.E. TRISTIMULUS VALUES BY THE WEIGHTED ORDINATE METHOD

This method requires transmittance data at equal 10 nm intervals from 400 nm to 700 nm, a total of 31 data points. Each transmittance value is multiplied by a weighting factor for X, another weighting factor for Y and a third weighting factor for A. There are thus three weighting factors for each of the 31 wavelengths. The products for each of the three C.I.E. primaries are then summed to give the three C.I.E. Tristimulus Values:

$$X = (T_{\lambda=1} \cdot fx_{\lambda=1}) + (T_{\lambda=2} \cdot fx_{\lambda=2}) + \text{———} (T_{\lambda=31} \cdot fx_{\lambda=31})$$

$$Y = (T_{\lambda=1} \cdot fy_{\lambda=1}) + (T_{\lambda=2} \cdot fy_{\lambda=2}) + \text{———} (T_{\lambda=31} \cdot fy_{\lambda=31})$$

$$Z = (T_{\lambda=1} \cdot fz_{\lambda=1}) + (T_{\lambda=2} \cdot fz_{\lambda=2}) + \text{———} (T_{\lambda=31} \cdot fz_{\lambda=31})$$

While this method required 85 multiplications and 3 additions, 2 of 31 terms each, and one of 23 terms, it is not too cumbersome using a desk calculator. Programmable electronic calculators make it even simpler and access to a time-sharing digital computer terminal makes it even quicker.

TABLE II

INTERLABORATORY VARIABILITY IN CALIBRATION FACTORS DETERMINED AT THREE APHA LEVELS

Participating Organization	Calibration Factors (F_n)* APHA 50	APHA 100	APHA 150
Allied Chemical	1373	1443	1485
American Aniline	**	1468	1441
American Cyanamid	1424	1440	1468
DuPont	1448	1455	1484
GAF	1364	1394	1439
Nyanza	1366	1400	1425
Rensselaer Color Lab	1348	1389	1427
Mean Values	1387	1427	1453
Pooled Variance	= 1055.2		
Standard Deviation	= ±32.5		
95 percent CL Single Value	= ±68.5	(APHA = ±4.9)***	
95 percent CL Mean of 7 values	= ±25.9	(APHA =±1.8)***	

* $Fn = \frac{(APHA)\ n\ b}{(DE)\ n}$

** Value discarded as cell path was too short for color value being measured.

***Estimates based on mean Fn determined at APHA 100.

An advantage of this method is that the transmittance data are at unit wavelengths which are easily and quickly set on a wavelength scale or read on the wavelength grid of a spectrophotometric curve.

Included is a work sheet (Table III) which gives the 93 weighting factors for C.I.E. 1931 Tristimulus Values, Source C. A worked example is included.

WORKED EXAMPLES OF CALCULATION OF C.I.E. TRISTIMULUS VALUES AND CONVERSION TO ADMI COLOR VALUES

The data used in the example calculating the C.I.E. Tristimulus Values by the Weighted Ordinate Method were taken from a transmittance curve obtained on a Cary 14 double beam spectrophotometer using as sample an NBS 2105 glass filter (2.93 mm). The C.I.E. Source C tristimulus values given by NBS for this filter are as follows:

$$X = 51.8 \pm 0.4$$
$$Y = 56.1 \pm 0.3$$
$$Z = 75.4 \pm 0.7$$

Also included in this Appendix is a worked example (Tables IV and V) of conversion of the C.I.E. Tristimulus Values (Selected Ordinate Method) to ADMI Color Value. This calculation assumes that the data were obtained on a solution measured in a 5 cm cell. Attention is drawn to the necessity of keeping track of the algebraic sign of the differences calculated.

TABLE III

WORK SHEET FOR CALCULATION OF C.I.E. TRISTIMULUS VALUES
WEIGHTED ORDINATE METHOD

Wave-length	%	X		Y		Z	
nm.	T	Factor	%T x Fact.	Factor	%T x Fact.	Factor	%T x Fact.
400		0.00108		0.00002		0.00513	
410		0.00329		0.00009		0.01570	
420		0.01238		0.00037		0.05949	
430		0.02997		0.00122		0.14628	
440		0.03975		0.00262		0.19938	
450		0.03915		0.00443		0.20638	
460		0.03362		0.00694		0.19299	
470		0.02272		0.01058		0.14972	
480		0.01112		0.01618		0.09461	
490		0.00363		0.02358		0.05274	
500		0.00052		0.03401		0.02864	
510		0.00089		0.04833		0.01520	
520		0.00576		0.06462		0.00712	
530		0.01523		0.07934		0.00388	
540		0.02785		0.09149		0.00195	
550		0.04282		0.09832		0.00086	
560		0.05880		0.09841		0.00039	
570		0.07322		0.09147		0.00020	
580		0.08417		0.07992		0.00016	
590		0.08984		0.06627		0.00010	
600		0.08949		0.05316		0.00007	
610		0.08325		0.04176		0.00002	
620		0.07070		0.03153		0.00002	
630		0.05309		0.02190		0.00000	0.00
640		0.03693		0.01443		0.00000	0.00
650		0.02349		0.00886		0.00000	0.00
660		0.01361		0.00504		0.00000	0.00
670		0.00708		0.00259		0.00000	0.00
680		0.00369		0.00134		0.00000	0.00
690		0.00171		0.00062		0.00000	0.00
700		0.00156		0.00056		0.00000	0.00
		X = Sum =		Y = Sum =		Z = Sum =	

TABLE IV
WORK SHEET FOR CALCULATION OF
C.I.E. TRISTIMULUS VALUES
WEIGHTED ORDINATE METHOD

Wave-length	%	X		Y		Z	
nm.	T	Factor	%T x Fact.	Factor	%T x Fact.	Factor	%T x Fact.
400	23.8	0.00108	0.0257	0.00002	0.0005	0.00513	0.1221
410	40.0	0.00329	0.1316	0.00009	0.0036	0.01570	0.6280
420	48.2	0.01238	0.5967	0.00037	0.0178	0.05949	2.8674
430	54.4	0.02997	1.6304	0.00122	0.0664	0.14628	7.9576
440	60.3	0.03975	2.3969	0.00262	0.1580	0.19938	12.0226
450	65.8	0.03915	2.5761	0.00443	0.2915	0.20638	13.5798
460	70.1	0.03362	2.3567	0.00694	0.4865	0.19299	13.5286
470	71.5	0.02272	1.6244	0.01058	0.7565	0.14972	10.7050
480	70.9	0.01112	0.7884	0.01618	1.1472	0.09461	6.7078
490	68.5	0.00363	0.2486	0.02358	1.6152	0.05274	3.6127
500	66.1	0.00052	0.0344	0.03401	2.2481	0.02864	1.8931
510	62.9	0.00089	0.0560	0.04833	3.0400	0.01520	0.9560
520	59.5	0.00576	0.3472	0.06462	3.8449	0.00712	0.4236
530	57.0	0.01523	0.8681	0.07934	4.5223	0.00388	0.2212
540	57.0	0.02785	1.5874	0.09149	5.2149	0.00195	0.1111
550	60.5	0.04282	2.5906	0.09832	5.9484	0.00086	0.0520
560	62.3	0.05880	3.6632	0.09841	6.1309	0.00039	0.0243
570	58.8	0.07322	4.3053	0.09147	5.3784	0.00020	0.0118
580	51.4	0.08417	4.3262	0.07992	4.1079	0.00016	0.0082
590	44.9	0.08984	4.0338	0.06627	2.9755	0.00010	0.0045
600	44.9	0.08949	4.0181	0.05316	2.3869	0.00007	0.0031
610	46.4	0.08325	3.8628	0.04176	1.9377	0.00002	0.0009
620	46.6	0.07070	3.2946	0.03153	1.4693	0.00002	0.0009
630	45.8	0.05309	2.4315	0.02190	1.0030	0.00000	0.00
640	44.8	0.03693	1.6545	0.01443	0.6465	0.00000	0.00
650	45.0	0.02349	1.0570	0.00886	0.3987	0.00000	0.00
660	43.4	0.01361	0.5907	0.00504	0.2187	0.00000	0.00
670	54.3	0.00708	0.3844	0.00259	0.1406	0.00000	0.00
680	63.0	0.00369	0.2325	0.00134	0.0844	0.00000	0.00
690	72.0	0.00171	0.1231	0.00062	0.0446	0.00000	0.00
700	79.1	0.00156	0.1234	0.00056	0.0443	0.00000	0.00
		X = Sum = 51.96		Y = Sum = 56.33		Z = Sum = 75.44	

TABLE V
WORK SHEET FOR CALCULATION OF ADMI
VALUES FROM C.I.E. TRISTIMULUS VALUES

C.I.E. Tristimulus Values	V_x	V_y	V_z	$(V_x - V_y)$	$(V_y - V_z)$
X_c = 98.00	9.900				
Y_c = 100.00		9.902		-0.002	
Z_c = 118.35			9.910		-0.008
X_s = 51.96	7.643				
Y_s = 56.33		7.841		-0.198	
Z_s = 75.44			8.263		-0.422

Step (1)	ΔV_y = 2.061		
Step (2)	$0.23\Delta V_y$ = 0.474	$(0.23\Delta V_y)^2$ =	0.225
Step (3)	$\Delta(V_x - V_y)$ = 0.196	$(\Delta(V_x - V_y))^2$ =	0.038
Step (4)	$\Delta(V_y - V_z)$ = 0.414		
Step (5)	$0.4\Delta(V_y - V_z)$ = 0.166	$(0.4\Delta(V_y - V_z))^2$ =	0.027
Step (6)		Sum =	0.290

Step (7) $DE = \sqrt{Sum} = \sqrt{0.290} = 0.539$

Calibration Factor (F) = 1.4×10^3

Cell Path Length, cm (b) = 5.0

Step (8) $$\text{ADMI Value} = F\frac{DE}{b} = \frac{(1.4 \times 10^3) \times (0.539)}{5} = 151$$

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