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THE COLOR OF WATER.

BY DESMOND FITZGERALD AND WILLIAM E. FOSS.

As many cities and towns are obliged to depend upon surface waters for their supplies, and as surface waters are liable to be discolored by the vegetable matter with which they come in contact, making them objectionable in appearance, it is important to have an accurate scale with which to measure the amount of the discoloration.

For several years past, this matter has received much attention upon the Boston Water Works. One of the principal sources supplying the city of Boston is that of the Sudbury River. The area of the water-shed above the point of taking, is about seventy-four square miles. On this area several large storage reservoirs have been built for the purpose of equalizing the yield of the streams. As the sites of the reservoirs have been mostly stripped of all organic matter, the effect of storage is to reduce the color of the water delivered by the feeders, but as it is impracticable to keep

the water in store long enough to decolorize it completely, much study has been given to the source and amount of the color delivered by the streams supplying the reservoirs. It has been found, as was expected, that the swamps and meadows were the principal sources of color.

In July, the color of the water coming from the swamps is a rich reddish-brown, and in the autumn, after the leaves have fallen, the color has more of a greenish cast.

The color of the brooks varies constantly during the year, depending largely upon conditions which cannot be now discussed. In winter the color is naturally low. In the spring the color is high, reaching its maximum in June, and a second maximum occurs in December.

In making plans for the improvement and drainage of the swamps it became important to be sure of the measurement of the colors, and as the color of the Boston water is almost an exact gauge of the organic matter which it contains, it also became important that the color of the water delivered to the consumers should be readily and accurately measured on some correct scale. It is the purpose of the writers of this article to consider here the matter of scale and methods of comparison.

When solar light is transmitted through a water containing foreign matter, some of its components are wholly or partially absorbed and the transmitted light is more or less colored in consequence. The color depends on the nature of the missing rays, or is the resultant of the rays which have been transmitted. The greater the depth of the water through which the light is transmitted, the greater will be the effect on the component and the more marked the color. Light which has traversed a depth of two meters of distilled water has only a very slight blue color, hence it can be said that in pure water all of the component colors are transmitted with almost equal facility.

The color standards at first used on the Boston Water Works were prepared by diluting portions of a highly colored water with distilled water until the colors matched those produced by nesslerizing varying amounts of an ammonia solution (0.01 Mg NH_3 per cc.) in fifty cubic centi-

meters of distilled water; the color being recorded as the number of cubic centimeters of the ammonia solution used.

These water standards are, therefore, as near as possible duplicates of the nesslerized ammonia standards employed for reading the color of water. They are much more convenient to use, because their color does not change as rapidly as that of the nesslerized ammonia solutions, which have to be mixed fresh at every observation. A set of standards having been prepared in the above manner, the color of a water is determined by comparison in Nessler tubes, which are of glass, about 15 to 20 millimeters in diameter and 300 millimeters in length and closed at one end. The tubes are filled with the different standards to a depth of 200 millimeters. A similar tube filled to the same depth with the water to be examined is moved along the scale until a point is reached where its color matches one of the standards. All of the tubes are viewed against a white background. When the color of the water falls between two consecutive standards, the color is estimated by the observer.

These natural water standards, although an improvement over the nesslerized ammonia standards, were found to be very unsatisfactory, for the following reasons:

They did not remain constant in color, but were found to change even when kept in the dark.

Standardizing a set against the nesslerized ammonia was very difficult, because the conditions when preparing a set of nesslerized ammonia solutions had to be always exactly similar in order to obtain uniform results.

It was also found that owing to irregularities in the scale the color of a water when diluted with distilled water would not vary with the dilution.

It was found that the platinum standard recently suggested by Dr. Allen Hazen* was not open to these objections, and was a much better standard to use.

"On the platinum standard the color of a water is the amount of platinum, in parts per ten thousand, which in

* *Amer. Chem. Journal*, Vol. XIV, No. 4.

acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water."

In preparing a set of standards, a standard solution having a color of 5.00 is usually prepared, and from this the lower standards are prepared by dilution with distilled water.

On this standard then, from the method of its preparation, the color of a water when diluted with distilled water will vary directly with the dilution.

The platinum standard which has been found to match the Boston water best, contains twenty-five parts of cobalt to fifty parts of platinum. It has been found to keep for months without change if protected from dust.

The method of comparing colors in Nessler tubes was not considered satisfactory. The color of a water falling between two consecutive standards depended largely upon the judgment of the observer. It was believed that a more convenient method could be obtained, and the colorimeter, shown on *Plate 1*, was designed to overcome these objections. *Plate 1* shows an isometric projection of the complete instrument and a section of the eye-piece. The latter consists of two totally reflecting prisms *A* and *B*, and a magnifying lens *C*. The lens is free to slide in the brass tube *D*, so that it can be focussed on the upper face of the prisms. The field of view is cut down to a circle by a diaphragm *E*, at the lower end of the tube *D*.

Rays of solar light from some uniform source, after passing through the water placed in tube *F*, which has a plate-glass end, enter the prism *A*, and emerging, illuminate one-half of the circular field of view.

Rays of light from the same source after passing through the standard solution in tube *G*, enter prism *B*, and are totally reflected at its surface, and emerging illuminate the other half of the field of view. The colors produced by the absorption of the two liquids can then be readily compared and brought to the same value, as follows:

The standard solution is held in a glass jar, and is connected by means of a glass tube with the standard tube.

The top of the jar is furnished with a piece of flexible

rubber tubing, terminating in an inflating bulb. By means of the latter the observer increases the depth of the standard solution in the standard tube, until the color produced on the field of view matches that of the water in the other tube; he then closes the pinch-cock on the tubing and reads the color of the water from the scale on the standard tube.

The color of a water determined by comparison in the colorimeter, should differ slightly from the color obtained by comparison in Nessler tubes and using the platinum standard, due to the fact previously mentioned that distilled water has a slight blue color. In the colorimeter the portion of the tube above the standard is not filled with distilled water, while in the Nessler tubes it is filled.

The following readings of a set of platinum standards in the colorimeter having some 1.00 platinum standard in the jar, are the average of two sets of readings by independent observers. They show that the maximum error does not exceed 0.02.

In cases where greater accuracy is required for water having a low color, a 0.50 standard should be substituted for the 1.00 in the jar.

<i>Platinum Standard.</i>	<i>Colorimeter Reading.</i>
0.10	0.115
0.20	0.22
0.30	0.32
0.40	0.40
0.50	0.50
0.60	0.595
0.70	0.70
0.80	0.80
0.90	0.895
1.00	1.00

The rapidity with which comparisons could be made by means of the colorimeter led to quite extended observation to determine the irregularities of the nesslerized ammonia and natural water scale already mentioned. On the lower portion of *Plate 2* these irregularities are illustrated graphically. The upper scale represents a uniform gradation, and the middle one the gradation corresponding to the nesslerized ammonia and natural water scales, and represents the

scale as determined by the average of observations made by two independent observers upon a set of natural water standards which had just been standardized against the Nessler solutions. The determinations were made with the colorimeter having some 1·00 natural water standard in the jar.

The lower scale shows the irregularities of the natural water and nesslerized ammonia scales as determined from the average of observations on fifteen sets of natural water standards made by three independent observers.

The differences between the two scales are probably due to the difficulty previously mentioned in preparing the nesslerized ammonia solutions and also to changes having taken place in the natural water standards after being standardized.

That the irregularities in the nesslerized ammonia and natural water scales are due to the method of preparation and not to any error introduced by the colorimeter, was shown by preparing a set of colors by diluting a 1·00 natural water standard with distilled water, and then reading these colors on the colorimeter, having some of the original 1·00 natural water standard in the jar. The following are the results:

<i>Dilutions of 1·00 Standard.</i>	<i>Reading on Colorimeter.</i>
·10	·095
·20	·21
·30	·295
·40	·405
·50	·52
·60	·60
·80	·80
1·00	1·00

From these investigations it was learned that the nesslerized ammonia and natural water standards were of very little value for accurate color readings.

To illustrate the misleading results obtained by using these standards, the following example may be taken:

Water having a color of 0·40 on the Nessler scale before filtration was found to have a color of 0·10 after filtration, showing a reduction of seventy-five per cent. by the process of filtration. By the uniform scale, however, shown

on *Plate 2*, this reduction is really only about fifty per cent.

Before the present form of the colorimeter was finally adopted, two methods were suggested by which the colors produced by the absorption of light by the standard solution and those produced by the water alone could be made to match.

The first was to vary the depth of the water under examination, while the depth of the standard remained constant. The second was to vary the depth of the standard, while the depth of the water remained constant.

A study of the first method showed that the depth of water could be varied between certain limits, only and that it was better, for accurate results, to keep the water under examination of a fixed depth. As the bottom of the tube is approached, the change in color, corresponding to any given decrease in depth of water, increases rapidly. It was decided that 200 millimeters would be the most convenient length for the tube, and that the scale divisions should not be less than two millimeters to be read accurately: also that a difference in reading of one scale division should not make an error in the resulting color of more than four per cent. It was also assumed for purposes of calculation that the color of the water and standard varied directly with the depth; that is, if the color of a water in a depth of 100 millimeters equals that of the standard in depth of 200 millimeters, then the color of the water would be twice that of the standard. If the color of the water in depth of twenty millimeters equals that of the standard in depth of 200 millimeters, then the color of the water would be ten times that of the standard.

The following table shows the increase of color corresponding to equal variation in depth of the water when a standard of 0.50 is used. It can be seen from the last column of this table how rapidly the differences of color, due to a decrease in depth of ten scale divisions, increases in the lower portion of the tube. It is thus evident that the readings of color in the upper portion of the tube

PLATE 2.

UNIFORM SCALE.

NATURAL WATER OR NESSLERIZED-AMMONIA SCALES.

will be of much greater accuracy than those in the lower portion :

Standard.	Depth of Standard. M. M.	Depth of Water. M. M.	Calculated Color of Water.	Difference of Color for 10 Scale Divisions.
0.50	200	200	0.50	—
"	"	180	0.55	.05
"	"	160	0.62	.07
"	"	140	0.71	.09
"	"	120	0.83	.12
"	"	100	1.00	.17
"	"	80	1.25	.25
"	"	60	1.67	.42
"	"	40	2.50	.83
"	"	20	5.00	2.50

In the upper diagram, Plate 2, the colors obtained by calculation have been plotted for several different standards; the abscissas represent the depth of water in the tube and the ordinates the calculated color when using the standard marked on each curve.

The cross on each of the curves shows the point at which the error in a color reading, resulting from an error of one scale division in reading, would equal 4 per cent. For all waters having colors darker than this, a new standard must be employed.

In this way it was found that where waters having colors ranging from 0 to 1.00 are common, at least three standards are necessary. For quick, practical work this method would be very inconvenient.

The second method, however, was found to have none of these objections; it gave readings of equal value in all parts of the tube, and readings from 0 to 1.00 could be obtained with a single standard, as shown by following table :

Standard.	Depth of Water. M. M.	Depth of Standard. M. M.	Calculated Color of Water.	Difference of Color for 10 Scale Divisions.
1.00	200	200	1.00	.10
"	"	180	.90	.10
"	"	160	.80	.10
"	"	140	.70	.10
"	"	120	.60	.10
"	"	100	.50	.10
"	"	80	.40	.10
"	"	60	.30	.10
"	"	40	.20	.10
"	"	20	.10	.10
—	—	0	0	—

The platinum standard has been adopted for use on the Boston Water Works.

For converting any former readings on the Nessler or natural water scale to the platinum, the following table can be used. It was prepared from observations on fifteen sets of natural water standards.

TABLE FOR CONVERTING COLORS ON THE NESSLERIZED AMMONIA AND NATURAL WATER SCALES, TO EQUIVALENT VALUES ON THE PLATINUM SCALE.

Natural Water Scale	'10	'20	'30	'40	'50	'60	'70	'80	'90	'100
Equivalent on Platinum Scale	'18	'26	'33	'39	'46	'52	'58	'63	'70	'81

For standards darker than 100 no satisfactory comparisons have yet been made. For reading colors darker than 100 it has been found best either to read in shorter depths or else dilute with distilled water in order to bring the color within the range of the 100 standard. The latter method has been adopted on the Boston Water Works. The reason for this is that it is often difficult to compare the dark waters with the standard owing to a difference of hue. It has been found that the amount of light which passes through a number of equal layers of an absorbing solution, diminishes in geometrical progression as the number of layers increase in arithmetical progression. Thus if I denotes the intensity of the incident light, Ia will be the intensity after transmission through unit thickness, where a is a proper fraction, and depends upon the nature of the substance and the refrangibility of the light employed. For a given wave length, a will be different for different substances; and for a given substance, a will vary with the wave length. The quantity a is termed the coefficient of transmission.*

It is because of the fact that the coefficient of transmission for the different rays varies with different solutions that we sometimes find a water matches the standard very closely in hue in a short depth, but appears of quite a different hue in a greater depth. This can be represented by a diagram as follows. Let the ordinates of the curve $a b c$

* Thomas Preston, *The Modern Theory of Light*.

in diagram, *Plate 3* represent the intensities of the incident rays of light from the red to the violet, which fall upon a water, and the standard with which it is compared. Then assuming the following coefficients of transmission for a depth of 100 millimeters.

	<i>Standard.</i>	<i>Water.</i>
Red	'1	'9
Orange	'5	'8
Yellow	'6	'6
Green	'9	'5
Blue	'9	'1
Violet	'9	'1

The intensities of the different rays after traversing 100 millimeters would equal their original intensity multiplied by their respective coefficients.

The intensities after traversing a depth of 300 millimeters would equal the original intensity multiplied by the third power of their respective coefficients giving the following:

	<i>Standard.</i>	<i>Water.</i>
Red	'001	'729
Orange	'125	'512
Yellow	'216	'216
Green	'729	'125
Blue	'729	'001
Violet	'729	'001

Plotting these values, gives the curves in the diagram. The upper curve shows the intensity of the different colors in the incident light, and the four other curves show the intensities after having passed through 100 and 300 millimeters of the standard and water respectively. Comparing the intensities after passing 100 millimeters of the water with those of the standard for the same depth, it is noticed that they do not differ much in hue or luminosity. Comparing the intensities after passing 300 millimeters of standard and water, it is noticed that the hue of the water has approached the red, while that of the standard has approached the blue.

These hues would therefore be quite different, and could not be accurately compared. The relative luminosity has also changed, the standard having become somewhat brighter than the water.

Color readings made by different observers, have been found to agree to within .02. Occasionally differences of .05 or more are found. These differences are usually found in cases where the water from turbidity or other causes differs from the standard in hue. This renders the comparison difficult, and the result depends largely upon the judgment of the observer.

The accuracy at present attained in color readings is probably quite sufficient for practical purposes.

The principal difficulty in the way of greater accuracy in color readings is the difference in hue between the prepared standard and the water. Maxwell, Young and Helmholtz claim that all color perceptions are due to the simultaneous excitation of three sets of nerve ends in the eye, and that all colors can be produced by a combination of three colors, red, green and blue in the proper proportion.

It is possible that a colorimeter might be constructed on this principle by employing standard red, green and blue solutions, so arranged that they could be combined in all proportions. A solution would also probably have to be employed to give the effect of turbidity to the standard.

With a colorimeter of this kind much more time would be required to make the comparison.

Prof. Ogden N. Rood* has employed these three constants to define completely a color.

- (1) Purity, or freedom from white light.
- (2) Luminosity, or brightness.
- (3) Hue, or wave length.

To measure the color produced by the absorption of a water it could be arranged so that the measurement of the first constant would not be necessary. The light after passing through the water, would consist of several components. It would be necessary to separate these by means of a prism or grating, and compare the spectrum thus obtained, with the spectrum of the original light. The measurements of the hues could then be accurately made, and the luminosity would remain as a photometric problem.

* *Text-Book of Color.* By Ogden N. Rood. 1892.

It appears, therefore, that in order to obtain much greater accuracy in color readings than is at present possible, more time and expensive apparatus must be employed. It would tend to uniformity of results and facilitate comparisons if all color readings were made on the uniform depth herein described, all water darker than 100 being diluted, as set forth on page 409.

One of the purposes of the writers of this article is to urge all chemists, analysts and others interested in matters of water supply to adopt the methods herein described, unless some better method can be found.

THE PHOSPHATES OF THE WORLD.*

BY FRANCIS WYATT, PH.D.

[Continued from p. 347.]

The cost of producing one ton of rock in dry marketable condition, is at the present moment generally allowed by the river companies to be about \$2.75 per ton, including fifty cents royalty to the State, and well-managed land companies with no royalty to pay, place their cost of production at from \$2.75 to \$3 delivered free alongside vessels in Charleston harbor.

Of the total annual output, about two-thirds of nearly all the land-rock, are consumed in the United States, principally in Charleston, Richmond, Baltimore, Philadelphia and New York; the river-rock, which constitutes the remaining third, is exported.

As a raw material of the first-class in the manufacture of soluble and available phosphates, South Carolina rock is everywhere held in the highest esteem. In Europe it is very popular, and, being of unvarying quality, has yielded results that cannot be surpassed by any other phosphate as an all-round staple, uniform and reliable article.

*A Lecture delivered before the Franklin Institute, January 12, 1894.