THE COLORING-MATTER OF NATURAL WATERS, ITS SOURCE, COMPOSITION AND QUANTITATIVE MEASUREMENT.

BY ELLEN H. RICHARDS AND J. W. ELLMS.

S O deeply seated in the mind of the average citizen is the prejudice against the amber-colored water of the most of the New England streams that it is only when reinforced by scientific authority that water boards and city councils are able to make any impression upon it.

It is only by actually filling up the well or by taking out the pump, that any Board of Health can prevent the use of a clear, cold, colorless, highly polluted well-water, no matter how abundant and free the tepid, turbid brown water supplied from the tap.

Color seems to have been associated in the popular mind with all sorts of hidden dangers. There lingers yet in memory the echoes of stories told to childish ears of the agonies suffered by those deluded persons who, in spite of the warning of their elders, persisted in drinking from wayside brooks and thus unwittingly swallowed what grew to be living monsters within them.

While there must be some ground for so strong and universal a feeling of danger, experience has certainly shown that a brown water from a carefully protected water-shed, when properly stored, yields a perfectly wholesome as well as most available and abundant source of supply.

It is said that the water from the Dismal Swamp is sought for by sailing vessels to take for three year cruises and many other brown waters have shown excellent keeping qualities after being stored for a time in clean basins to allow of the sedimentation of the extraneous matter which may have been carried along by streams.

The source of brown color in natural surface waters is to be found in the decaying elm, maple, oak, and other leaves which carpet the hillsides and swamps each autumn, and in the surface soil, which everywhere, and particularly in the lowlands, is rich in peaty or " humus " matter.
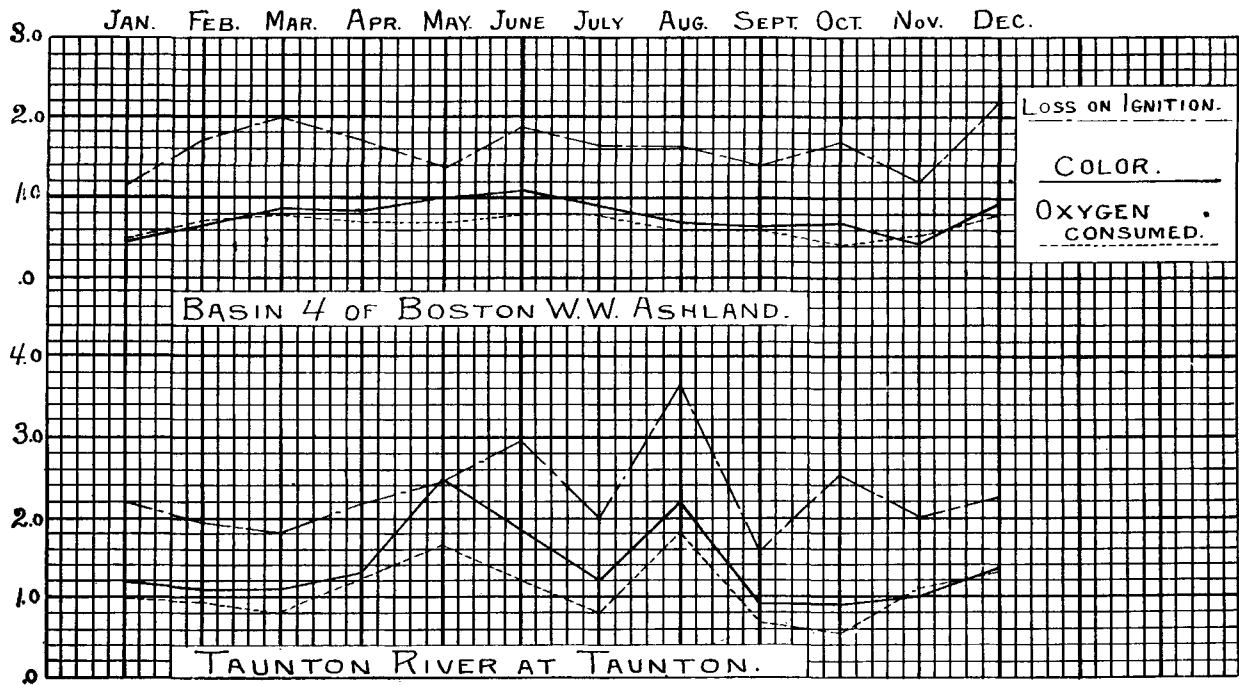
CHART I.

The chlorophyl derivatives, glucoses, and glucosides dissolve out of the fallen leaves in the early autumn, giving a light yellow color to the brooks, but after soaking all winter, mostly under the ice and snow, the leaves yield to the warm spring rains a rich deep brown liquid which is exactly what Thoreau, with poetic instinct, called it, namely " meadow tea." It is at least as harmless as Japan tea. The coloring-matter in both cases is due to the slow carbonizing of the leaf and the formation of soluble compounds rich in carbon.

The variation in the depth of color of brown surface water at different seasons of the year, is well shown in chart 1. The color curve plotted for basin 4 of the Boston Water Works, in Ashland, for a year, shows the steady rise in color from January to June, and then a falling off toward the latter part of the year. This is a typical, unpolluted surface water. Taunton river, on the other hand, receives drainage from a variety of sources as well as from the neighboring swamps, and shows greater fluctuations.

When any organic substance as wood, leaves, and the like, is treated with strong sulphuric acid, a decomposition occurs more or less complete ; and the result is, according to the strength of the acid and the temperature at which it is applied, either a mass of nearly pure carbon or a gummy substance soluble in water with the production of a deep brown-colored solution. When sugar is gently heated it parts with a portion of the elements of water, becoming richer in carbon as the process is pushed farther. The result is a brown substance known as " caramel " soluble in water ; there also may be produced various less soluble compounds, depending on the temperature used, which have been at times called caramelane, caramelin, and caramelene.[1]

But the most instructive instance of the production of this characteristic brown substance is, perhaps, in the case of the well known colorimetric determination of carbon in steel. By using Stead's alkali method, a soluble brown color is obtained which compares very closely with the color of the dark brown waters under consideration. Whether an estimation of the

[1] Peligot. *Ann. chim. phys.* [2], 67, 172 ; Völckel. *Ann. Chem.* (Liebig), 85, 59 ; Maumené. *Compt. rend.*, 39, 422 ; Graham. *J. Chem. Soc.*, 15, 258.

actual quantity of carbon in these coloring-matters can be made, is yet to be determined.

The color in solutions from all these sources may be removed with milk of alumina, may be precipitated by barium hydroxide, and in all cases the solutions are decolorized by the action of potassium permanganate, indicating the complete oxidation of the color-giving compound of carbon. All are comparable in color when matched in tubes or read in the tintometer to be described.

These facts all indicate that this brown color is imparted to aqueous solutions by the same compound of carbon or by closely related compounds.

In the coloring-matter of surface waters there are, most probably, several complex substances, among them tannins, glucosides, and their derivatives, out of which it seems almost hopeless to attempt to isolate any one which may be said to be the substance under consideration. Some of these decomposition-products contain iron and it has been suggested that the color-giving compounds may result from the breaking up of chlorophyl.[1] That iron is not essential to the formation of the color is shown by the fact that the brown color may be given by a solution of caramel made from pure sugar, and that iron may be absent from the carbon color obtained from steel, but it is true that a very small quantity of iron does, as a rule, accompany the brown color of natural waters.

Since any colored natural water gives a certain proportion of albuminoid ammonia, increasing as the color increases, it would seem that the color compound might contain nitrogen. The following are results of experiments tried some years ago :

	Color.	Albuminoid ammonia.
(1) Peat solution ················ ···	2.0	0.0516
(2) Fresh leaf solution···············	0.8	0.0494
(3) Second extract of same leaf ·······	0.8	0.0174
(4) An old leaf repeatedly extracted with water·····················	0.9	0.0072

It will be seen in the two leaf solutions (2 and 3) with the same color of eight-tenths there is a reduction of 64.7 per cent. in the nitrogen and that with a color of one-tenth more in the

[1] F. S. Hollis, Report of the Boston Water Board, 1892.

old leaf solution (4) there is 85.4 per cent. less nitrogen than in the fresh leaf solution (2). While it is possible that the color-giving compound or compounds contain nitrogen as an essential constituent, it is evident that a large diminution in the nitrogen does not produce a corresponding lessening of the color.

The following figures show the carbon, hydrogen, and nitrogen contained in (1) the residue of Boston tap water, (2) a very dark-colored water from Cedar Swamp, Westboro, and (3) humic acid extracted from soil.

	Carbon.	Hydrogen.	Nitrogen.
Boston tap water[1]	30.71	5.96	7.68
Cedar Swamp water[1]	43.72	3.92	4.82
Humic acid[2]	50.4	4.8	3.6

No attempt has been made by us to give a more definite formula for these apparently highly carbonaceous compounds since so little seems to be known of the reactions attending the gradual carbonization of such organic substances. It is probable that one of the compounds may be what is known to the agricultural chemist as humic acid or humus matter. Berthelot finds a close relation between this substance prepared from peat and from sugar, only the latter is free from nitrogen.

QUANTITATIVE MEASUREMENT.

Formerly the brown color of water was supposed to be a bar to its use for domestic purposes and analysts sought for some standard of comparison by which to set a limit of allowable color. One of the early methods was by the determination of the quantity of oxygen consumed or absorbed from potassium permanganate, either hot or cold in acid or alkaline solution. If the substance which gave the brown color had a known composition so that any given percentage of oxygen consumed could be said to correspond to a definite quantity of the carbonaceous compound, this might be a valuable standard. The fact is, however, that at present the results are often misleading, since a highly polluted water may give much lower results than a dark brown water which by years of use has been shown to be perfectly wholesome.

1 H. T. Gallup, Thesis, Mass. Inst. Tech., 1894.
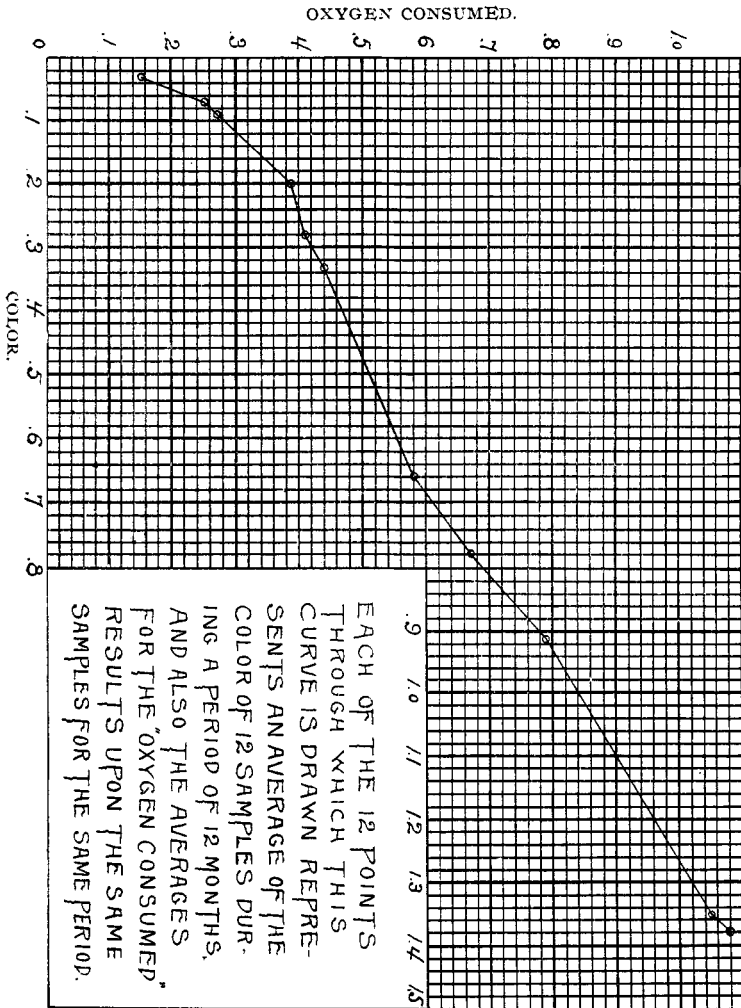2 Berthelot: *Compt. rend.*, 569 *1892*, .

OXYGEN CONSUMED.

CHART II.

EACH OF THE 12 POINTS THROUGH WHICH THIS CURVE IS DRAWN REPRESENTS AN AVERAGE OF THE COLOR OF 12 SAMPLES DURING A PERIOD OF 12 MONTHS, AND ALSO THE AVERAGES FOR THE "OXYGEN CONSUMED" RESULTS UPON THE SAME SAMPLES FOR THE SAME PERIOD.

Since not all carbon compounds are affected by this treatment and since the organic matter in solution is probably made up of several substances having quite different composition, it is not surprising that we have thus far failed to establish a definite relation between the quantity of organic matter present and the oxygen given up to it by the potassium permanganate. In a

general way, a rise in color is followed by a rise in the oxygen consumed, as is shown by the diagram on chart II.

As soon as the fact was recognized that fixed standards could not be rigidly applied to all waters from all sources, and that a certain quantity of albuminoid ammonia invariably accompanied the brown color of perfectly wholesome water and somewhat in proportion to the color,[1] it became of importance to be able to estimate the relative depth of color in waters. For this some standard was of course required. Various substances have been proposed from time to time, such as solutions of caramel, and metallic solutions[2] of various kinds. Largely on account of its convenience as being always in use in the laboratory and because the colors matched easily, the method originally suggested by Prof. A. R. Leeds,[3] namely, the use of the nesslerized ammonia standards, was at first adopted in the Laboratory for Water Analysis of the Institute of Technology.

It occurred to one of us[4] to prepare considerable quantities of water of the various depths of color most frequently met with in ordinary routine work, and to use these as standards of comparison, of course based upon the ammonia standards made with a Nessler solution which gave a sufficiently brown tint. An additional advantage to that of having them ready at a moment's notice was that the colors were identical and no mental effort was necessary to eliminate the slight differences in tint which almost of necessity occurs when two substances of unlike composition are compared.

Natural water standards when so prepared fade in time like the caramel solutions, even when carefully covered from the light, and, although sterilized at first, the bottles cannot remain so when opened for daily use, so that a freshly standardized set is required as often as once in six months. It is well known that the Nesslerized ammonia standards vary considerably as prepared in different laboratories because of the different methods of making up the Nessler solution, and it was very desirable

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[1] T. M. Drown. The Interpretation of Analyses, Mass. State Board of Health Report, 1890, p. 566.

[2] Crookes, Odling & Tidy. *Chem. News*, **43**, 174 ; Hazen; *Am. Chem. J.*, **14**, 300.

[3] Proceedings Am. Chem. Soc., **2**, 8.

[4] Mrs. E. H. Richards, Mass. State Board of Health Report, 1890, p. 532.

to find some standards of absolute quantitative value, which could be applied anywhere, and which would give comparable results.

Many chemists have found the metallic standard of platinum and cobalt satisfactory for tests for the working of filters and where only low colors are dealt with ; but for the wide range of colors met with in our work, some 500 numbers from 0.01 to 5.00, we cannot match two such different combinations of colors with any degree of accuracy in the higher portions of the scale.

The reason is evident, and it is equally patent in all forms of color measurement ; '' for color is not a simple physical quantity like weight of temperature, but a physiological effect which varies with individual peculiarities and bears no very simple relation to the physical causes which produce it."[1]

The constituents of the resulting matched colors also may be very different and one may vary more than the other under varying conditions of light, depth of column, and density.

There is a wide field for experiment in the physics of color-measurement in solution and which in view of the increasing use of such methods in quantitative determinations is of extreme importance to chemists. Without going into detail on this point, one instance may be cited. It has been observed in matching Nessler standards that the readings are exact only within certain limits; for instance, colors higher than those given by four cc. of standard ammonia, 0.00001 gram in one cc. observed in a column of nine inches in depth, are very difficult to compare, and as the quantity of ammonia increases the color becomes more and more red until the point of precipitation is reached. That is, the normal eye is more sensitive to certain shades of color than to others and there is a limit to the depth of color which can be correctly estimated. Also, while one solution may appear redder than another in a deep column it may appear less red in another of a less depth. For example, a natural water standard of color, 5.0 on the Nessler scale contains only 0.0005 per cent. dissolved organic matter. A solution of carbon from steel, prepared by Stead's[2] method, is

1 H. R. Proctor: *J. Soc. Chem. Ind.*, 14. 2.
2 J. Iron and Steel Inst., 1883, p. 213 ; also Blair's Iron Analysis, p. 170.

strongly alkaline and contains twenty per cent. dissolved salts. A solution of caramel is nearly the same in character as the water, and a strongly acid solution of platinum and cobalt contains two-tenths per cent. of salts.   If these solutions are matched as nearly as possible by the eye in nine-inch tubes and then the tintometer readings are taken, it is found that the ratio of orange to excess of yellow in the water standard is as one to 1.21, or the color is yellow orange.

The ratio in the solution of the carbon from steel is one to 1.38, or a slightly yellower orange ; the ratio in the caramel is one to 1.42, while in the platinum cobalt it is one to 1.6, or a decidedly yellow orange.

It will be evident therefore, why an optical instrument of precision which promised to furnish a universal standard applicable anywhere, was eagerly welcomed.

The tintometer devised by Joseph W.Lovibond, of Salisbury, England, was examined by Dr. T. M. Drown in the inventors laboratory, and an instrument was imported for the use of the State Board of Health.

It consists of two tubes side by side with openings at one end and divided by a central taper partition terminating with a knife edge at the eye piece, which it divides equally in such a way that on looking through the eye piece the two openings are simultaneously visible.   The liquid is placed in cells of definite lengths, one inch, two inches, up to twenty-four inches.   The standards consist of three sets of graded colored glasses, red, yellow and blue, numbered according to their depth of color.

" By using several superimposed glasses from a set, a depth of color is represented by the aggregate of tint number on the glasses used, whilst glasses from different sets produce a composite color, and the exact proportion of each component color can be read off."

The use of the Lovibond instrument in our hands has been confined first, to the determination of the color scale which has been in use for the past eight years in the laboratory for water analysis of the Institute of Technology, and by which the numbers found in the reports of the Mass. State Board of Health, in the tabulated result of 15,000 samples, have been obtained ; and

secondly, to a color comparison of some other substances in order to find some standard by which a quantitative estimation of the carbon present may be made.

The natural water color standards are prepared by dilution of a highly colored surface water with distilled water. At certain points in the scale the dilution is such that when the colors are read in 50 cc. tubes they match Nesslerized ammonia (0.01 mg. ammonia per cc.) standards read in the same volume and depth (23.5 cm.) The points in the scale at which this matching is made are at 0.2, 0.5, 1.3, 1.8 and 2.0.

Above the color standard of 2.0 the scale is prepared by dilution of the highly colored water in such a manner as to have the quantity of color proportionate to the depth in which the reading is made. For example, a color of 4.0 is prepared so that when read in one-half the usual depth, (*i. e.*, 11.75 cm.) it matches a color of 2.0 read in the full depth (23.5 cm.).

From the color 0.00 (distilled water) up to 0.2, and for the intervals between the points matched against the Nesslerized ammonia standards, the gradation is made by the eye.

The standard colors to be measured by the tintometer were prepared in this way, and were read in four different lengths of cell. Colors from 0.00 in the scale to 0.3 inclusive, were read in a twenty-four inch cell, from 0.3 to 1.5 in a six inch cell, from 1.5 to 4.0 in a two-inch cell, and from 4.0 upwards in a one inch cell. This method permitted the readings for the " standard yellow glasses " to be kept within 4.0 of the tintometric scale. This is desirable for the reason that the eye is liable to be less sensitive in reading above 4.0 of the "yellow standard glasses " than below that limit.

The following condensed table (No. 1.) gives the readings of the laboratory standards. The measurements are tabulated for convenience in units of yellow, red and blue of the tintometric scale. It must be understood, however, that the color transmitted to the eye when red and yellow glasses alone are used, and when the number of units of yellow exceed those of the red, is orange mixed with yellow. If yellow and blue glasses are used together, the color transmitted is violet with a mixture of blue or yellow,

as the case may be, depending upon the preponderance of one or the other of those colors. A neutral tint unit is obtained by a combination of three equal color units. Therefore, if the three colors are used, black or a decrement of normal white light is obtained.

TABLE NO. 1.

READINGS OF THE TINTOMETER "STANDARD GLASSES" FOR YELLOW, RED AND BLUE, WITH THE DIFFERENT LENGTHS OF CELLS USED.

	Natural water standard color scale.	Yellow.	Red.	Blue.	Yellow.	Red.	Yellow.	Red.	Yellow.	Red.
Section 1. Color of water measured in a cell 24 inches in length.	0.00	0.40		1.00						
	0.05	0.90		0.20						
	0.10	1.20	0.10							
	0.15	1.90	0.32							
	0.20	2.40	0.84							
	0.30	3.50	1.05		0.80	0.30				
Section 2. Color of water measured in a cell 6 inches in length.	0.40				1.10	0.42				
	0.50				1.35	0.58				
	0.60				1.60	0.66				
	0.70				1.85	0.80				
	0.90				2.40	1.10				
	1.00				2.70	1.25				
	1.20				3.20	1.55				
	1.30				3.50	1.70				
	1.50				3.90	1.85	1.20	0.60		
Section 3. Color of water measured in a cell 2 inches in length.	1.80						1.35	0.70		
	2.00						1.50	0.80		
	2.50						1.95	1.00		
	3.00						2.50	1.20		
	4.00						3.20	1.60	1.60	0.80
Section 4. Color of water measured in a cell 1 inch in length.	5.00								1.95	1.00

If the color sensations were transmitted uniformly, then, having obtained a reading in a given length of cell for a color of 0.2 a color of 0.6 would give three times as much yellow and three times as much red, and a color of 1.8 would give nine times as

much yellow and nine times as much red, but as a matter of fact the actual reading shows sixteen times as much yellow and eight and two-tenths times as much red.

The following table will show this more distinctly :

READING OF 0.2 COLOR IN TWENTY-FOUR INCH CELL = 2.40 YELLOW, 0.80 RED.

		Calculated readings.		Observed readings.	
		Yellow.	Red.	Yellow.	Red.
Color	0.6	7.20	2.40	7.60	2.40
"	1.0	11.00	4.00	15.53	3.65
"	1.8	22.80	7.20	38.49	6.60

Therefore, in the case of a higher color a shorter length of cell is used, so that the readings may be always made with lighter colored glasses.

The second table (No. 2) represents the differences for each tenth of color in the natural water standard scale, beginning with 0.00 and running to 5.0, as measured by the tintometer "standard glasses" for both yellow and red. In one column is shown the estimated difference for yellow and red, if the increase in any section were proportional to the numerical increase of the natural water standard scale. The basis for calculation is arbitrary for each section. (The section here is the division made by reading in the different lengths of cell.) The basis of calculation for the first section (twenty-four inch cell) is the color standard (0.1) which reads yellow 1.20, red 0.10. For the six inch cell the color 0.3 which reads yellow 0.80, red 0.30. For the two inch cell, the color 0.5, which reads yellow 1.20, red 0.60, and for the one inch cell, the color 4.0 which reads yellow 1.6, red 0.80. It will be seen that the estimated and observed differences agree quite well and indicate a regular increment of color as the scale ascends.

Considering the fact that we have had the instrument in our hands for a few months only and that we have been able to give to it only the odds and ends of time which a full daily routine left at our disposal, and therefore, that we cannot claim to have as yet perfectly trained eyes, the results are very encouraging, especially as in the case under consideration, we have to deal with a mixture of very impure colors.

TABLE NO. 2.

DIFFERENCES IN THE TINTOMETRIC READINGS OF RED AND YELLOW FOR EACH TENTH OF COLOR IN THE NATURAL WATER STANDARD SCALE.

	Natural water standard color scale.	Yellow.		Red.		Estimated difference.
Sec. 1. Color of water measured in a twenty-four inch cell.	0.00					
	0.10	0.80				Yellow = 1.20
	0.20	1.20		0.74		Red = 0.10
	0.30	1.10		0.21		
Sec. 2. Color of water measured in a six inch cell.	0.40	0.30		0.12		
	0.50	0.25		0.16		
	0.60	0.25		0.08		
	0.70	0.25		0.14		
	0.80	0.275 } 0.55		0.15 } .30		
	0.90	0.275		0.15		
	1.00	0.30		0.15		Yellow = 0.27
	1.10	0.25 } 0.50		0.15 } 0.30		Red = 0.10
	1.20	0.25		0.15		
	1.30	0.30		0.15		
	1.40	0.20 } 0.40		0.075 } 0.015		
	1.50	0.20		0.075		
Sec. 3. Color of water measured in a two inch cell.	1.60	0.05 }		0.033 }		
	1.70	0.05 } 0.15		0.033 } 0.010		
	1.80	0.05 }		0.033 }		
	1.90	0.075 } 0.15		0.05 } 0.10		
	2.00	0.075		0.05		
	2.10	0.09		0.04		
	2.20	0.09		0.04		
	2.30	0.09 } 0.45		0.04 } 0.20		
	2.40	0.09		0.04		
	2.50	0.09		0.04		
	2.60	0.11		0.04		Yellow = 0.08
	2.70	0.11		0.04		Red = 0.04
	2.80	0.11 } 0.55		0.04 } 0.20		
	2.90	0.11		0.04		
	3.00	0.11		0.04		
	3.10	0.07		0.04		
	3.20	0.07		0.04		
	3.30	0.07		0.04		
	3.40	0.07		0.04		
	3.50	0.07 } 0.70		0.04 } 0.40		
	3.60	0.07		0.04		
	3.70	0.07		0.04		
	3.80	0.07		0.04		
	3.90	0.07		0.04		
	4.00	0.07		0.04		
Sec. 4. Color of water measured in a one inch cell.	4.10	0.035		0.02		
	4.20	0.035		0.02		
	4.30	0.035		0.02		
	4.40	0.035		0.02		
	4.50	0.035 } 0.35		0.02 } 0.20		Yellow = 0.04
	4.60	0.035		0.02		Red = 0.02
	4.70	0.035		0.02		
	4.80	0.035		0.02		
	4.90	0.035		0.02		
	5.00	0.035		0.02		

Table No. 1 will at least serve as a rapid method for the standardizing of the stock bottles of natural waters, as the observer's eye becomes trained and more knowledge is obtained of the conditions which influence readings, a more perfect scale may be constructed.

The direct use of the instrument with the construction of a chart for each water, is evidently out of the question where, as in our laboratory, the color must be determined on twenty or thirty samples a day.

A modification of the tintometer has been proposed by H. R. Proctor, Yorkshire College, Leeds, England.[1]

This is designed to bring the color patches into juxtaposition as is done in the comparison of two spectra instead of having the separating dark band in the centre. We have not been able to try this instrument, but it promises to be an improvement.

ON THE ESTIMATION OF LEVULOSE IN HONEYS AND OTHER SUBSTANCES.

BY H. W. WILEY.

A SIMPLE optical method for the estimation of levulose is of great advantage in the examination of honeys and other substances containing that body. The following optical method is one of easy application when the analyst has access to the jacketed observation tube, which will be mentioned below.

The principle of the process rests upon the change in the specific rotatory power of levulose at different temperatures. The change in the optical rotation of other bodies associated with levulose in the conditions of the experiments to be described is so little as to affect the data obtained to a very slight degree. The process, as it has been worked out, is easily applied and gives results which it is believed are better than those obtained by any other method.

The Observation Tube.—The most important adjunct of a mechanical nature in the process is an observation tube which