assay as well as the character of the mixture and of the samples analyzed, I do not believe the analyst would be justified in reporting any *exact* amount of oleostearin found and have therefore adopted the form of reporting that the sample submitted contained "not less than —— per cent., nor more than —— per cent.," the margin of the error being as stated.

UNITED STATES LABORATORY.

THE MEASUREMENT OF THE COLORS OF NATURAL WATERS.

BY ALLEN HAZEN.

Received January 30, 1896.

THE diffusion of more accurate information and more rational theories as to the causation of diseases during the past few years has resulted in simplifying and changing many of the problems presented in connection with the chemical analysis of public water supplies. The healthfulness of a water for such use is determined to a much greater extent than formerly, by critical inspections of the sources of supply, particularly in the case of surface waters; and information as to the size of the water shed, flow at different seasons, amount of storage and character of the storage reservoirs, together with full information in regard to the population on the water shed and the way it disposes of its sewage, are more important and frequently adequate in themselves to determine the wholesomeness or unwholesomeness of a water; and the use of chemical analysis in connection with the investigation of such problems is rather in serving as an index of the varying amounts of contamination at different times, than in showing the presence or absence of substances which are in themselves injurious to health. Bacterial examinations also, which have become so frequent and necessary in connection with analyses of this character, play also their part in measuring such fluctations.

There are, however, several determinations which indicate in themselves substances desirable or undesirable in a public water supply, and among these perhaps the most important are the hardness, the color, and in the case of ground water supplies, the iron; and although the color is determined mainly for its own sake, and because a colorless water is more desirable than a colored water, and not because of any direct relations that the results obtained may bear to the wholesomeness of the supply, the interest that attaches to the determination often makes it of no less importance than those of the ammonia or other organic constituents.

The importance of this question of color has long been felt, and numerous efforts have been made to devise means for measuring and recording the colors. The essential requirements of such a method are that the figures obtained for a given color shall be the same at all times and in all places, and that it shall be possible to reproduce the colors with certainty at any future time. It is also desirable that the figures obtained shall be as nearly as possible proportional to the actual apparent colors of the various waters, as seen under ordinary conditions.

Perhaps the simplest method of measuring the colors of waters consists in taking a solution with a color of substantially the same hue as the waters to be examined, and diluting it with various quantities of distilled water, producing a series of colors with which the waters may be compared and results of relative colors obtained. The most natural substance to use for the colored solution is a highly colored swamp water, but the results obtained with such a standard of color, although comparable among themselves, would hardly have further permanent value owing to uncertainty as to the color of the water used for comparison, and the certainty that this color would fade, and the impossibility of reproducing it with accuracy at a future time. It is evident that any such procedure cannot fairly be considered as establishing a standard of color, and that the colors must have some definite physical basis which can be formulated and described with certainty and which will allow them to be reproduced at pleasure.

Perhaps an ideal basis of description of color would be a statement of the changes in the numbers and intensities of the vibrations in white light produced by passing through a layer of the water under examination. These changes are, however, so hopelessly complex as to defy even the hope of ascertaining them, and even if they could be determined it is doubtful if a statement of them could be made simple enough to convey any meaning to the ordinary mind as to the colors represented.

The most satisfactory standard which we can reasonably hope to realize is probably furnished by some other substance with a definite color, which can be produced at will, and which can be compared with the colors of waters, furnishing results of permanent value. One of the first attempts at such a standard was made by Messrs. Crooks, Odling, and the late Dr. Tidy,[1] who used solutions of ferric and copper salts in solution in independent vessels, which, superimposed upon each other, produced a color equivalent to that of the water. The fatal objection to this standard was that the color of the iron solution depends very largely upon the formation of basic compounds which vary in the intensity of their colors with very slight variations in acidity and with changes in temperature, so that the results obtained are open to a most objectionable uncertainty.

Another, and in some respects more satisfactory, attempt in establishing a standard was made by Prof. A. R. Leeds,[2] who suggested that extremely dilute solutions of ammonia after being nesslerized should be taken as the standards of color, the quantity of ammonia being taken as an index of the color produced. This standard was certainly most convenient, as the nesslerized ammonia standards are always present in laboratories for water analysis being required for another purpose, and it was believed that the colors had a sufficiently definite value to form a reliable standard.

This method has been widely used in the United States, and was employed by the author for several years and for the examination of some thousands of samples of water, until it became apparent that the variations and discrepancies in the results obtained were so great as to require serious consideration. As a result, a critical examination of the colors produced in this way was undertaken with the aid of my then assistant, Mr. Harry W. Clark, the results of which were published in full in the *American Chemical Journal*, **14**, 300. It was found in the course of the investigation that the colors produced depended not only upon the amount of ammonia used, but also upon a

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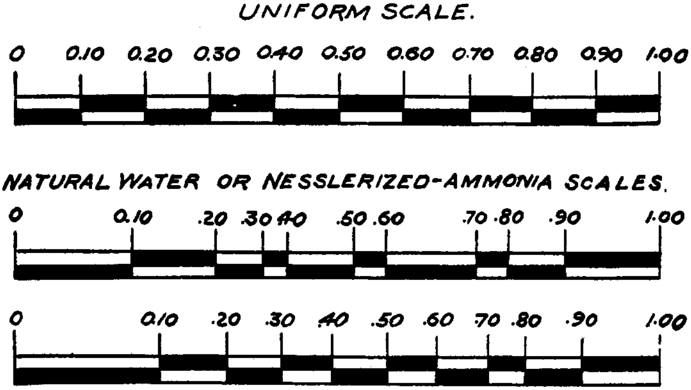
[1] *Chem. News*, 43, 174.

[2] *Proc. Am. Chem. Soc.* 2, 8.

whole series of conditions, many of which were not capable of exact control, so that the results obtained varied among themselves, even in the same laboratory at different times, to a most unsatisfactory extent. It was found that the colors produced depended not only upon the composition of the Nessler reagent and the quantity used, but even upon the way in which it was applied to the water containing the ammonia, and to a very large extent upon the temperature at which the experiment was made. It was further found that the colors produced were not at all proportional to the quantities of ammonia present, even under the most favorable conditions, owing in part to the very considerable color of the Nessler reagent itself, and in part to the fact that small amounts of ammonia produce less color relatively than larger quantities ; and as a result of the combination of these two causes the colors increase in an irregular way that is most unsatisfactory. This irregularity of increase is well shown by a cut here reproduced from the report of Mr. FitzGer-



Irregularities in Nesslerized Ammonia and Natural Water Standards: From Report by Mr. FITZGERALD and Mr. FOSS in Report of BOSTON WATER BOARD for 1893.

ald and Mr. Foss in the report of the Boston Water Board for 1893,[1] showing the colors of nesslerized ammonia and natural water standards received from the Institute of Technology when read against a single natural water standard in an ingenious colorimeter devised by the authors, and in addition the difference between the two lower scales shows how the standard differed at two different times.

The nesslerized ammonia standard has been improved in an important way by Mrs. Ellen H. Richards, of the Massachusetts Institute of Technology, who has for some years used standards of natural waters diluted with distilled water, as suggested above, and diluted to such an extent as to correspond with the nesslerized ammonia standards at a number of selected points, and with intermediate and lower standards prepared by interpolation between the selected points of comparison. This method of procedure eliminates to a certain extent the daily fluctuations in the values of the nesslerized ammonia standards, and also tends to smooth out the smaller irregularities in the scale, although the larges ones could hardly be removed without destroying the integrity of the scale itself. The method of procedure is, moreover, open to the more serious objections to the nesslerized ammonia standard in that the standards themselves depend for their original values upon the nesslerized ammonia standards of which the exact values are always open to question.

In a recent article published in the present volume of this Journal, page 68, by Ellen H. Richards and J. W. Ellms, an account is given of an attempt to establish in a more accurate and permanent manner the value of the standards used by comparing them with the Lovibond "Tintometer." This instrument consists essentially of a series of colored glasses which are superimposed upon each other to produce a color equivalent to that of a given sample of water or other substance. The tintometer in its construction and operation is so complicated as to render it impracticable, as Mrs. Richards states, to use it for the direct determination of colors in waters where many samples have to be examined, and its use is thus limited to determining

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[1] *Franklin Institute*, **138**, 401.

from time to time the values of the standards actually used for measuring the colors which would otherwise be subject to uncontrolled variations.

Several objections may be raised to the use of the Lovibond Tintometer as an ultimate standard of color. If we admit that the colors of the glass slips are permanent and will forever hold their color, we still depend upon the honesty and skill of the manufacturer of the instruments to produce glass slips of precisely the same values as those used in the original apparatus. It is of course conceivable that an apparatus should be continued in use with the same slips for many years, but eventually the slips would become worn or scratched and would require to be replaced, or the apparatus might be destroyed by fire or other accident; and in any case other laboratories buying new instruments will require to have new slips. It is thus seen that the values of the colors depend ultimately upon the honesty and skill of the manufacturer in preserving and reproducing an arbitrary standard, and not upon natural units.

It may be said as against this view that the values of the Lovibond units have been determined by comparison with the colors of solutions of definite chemical composition with such care and precision that it will be possible at future times to determine whether the slips then in use are really the equivalents of those now sold, and that it would even be possible to reproduce them in case the present standards were lost or destroyed. But against this statement it may be urged that it is much more rational, simpler, and better in every way to compare the waters directly with the chemical solutions which are the ultimate points of reference without the intervention of glass slips or other standards.

An attempt to do this was made by the author, who published[1] a description of a method of comparing the colors of waters with those of solutions of platinum and cobalt of known strength, the colors of which were absolutely definite and permanent, and capable of being reproduced with precision at any time, and not affected by temperature or other conditions likely to occur in well regulated laboratories. The method of stating the results

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[1] *Am. Chem. J.*, 14, 300.

was a natural and simple one, namely, "that the color of a water is the amount of platinum, in parts per ten thousand which, in acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water."

Since the publication of this article the platinum standard has been used in laboratories under my direction, and by my successors, and in other and independent laboratories for the measurement of colors in many thousands of samples of water, and with such uniformly satisfactory results[1] that I believe it only fair to say a word in regard to the objections raised to the standard by Mrs. Richards in the above mentioned article.

The first of these objections is that there is an excess of orange to yellow in the standard, which, if I understand the language correctly, means that the standard is redder than the waters to be examined. This contingency was provided for in the original article by making the platinum the standard of color and allowing the cobalt to be varied as required to match the hues of the waters. The quantity of cobalt in proportion to the platinum which I suggested, namely, one-half as much metallic cobalt as platinum, was the result of my experience of thousands of samples of water prior to the publication of that article, but as waters from different sources vary in their hues, it was fully recognized that it might be desirable in other cases to use a different proportion of cobalt from that suggested; and if it is found that the quantity of cobalt suggested produces a standard too red for a given set of waters, it is only necessary to make a fresh standard with a somewhat smaller quantity of cobalt to be determined by experiment, when it will be found that the hue matches the waters as closely as it is possible for any single standard to do.

As a matter of fact, standards containing a quarter less and others containing a quarter more cobalt than the amount suggested have been repeatedly used by the author and by others for special purposes, and, while the hues of some waters are more accurately matched, the results as a whole have hardly warranted any change in the proportion suggested for ordinary practical work.

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[1] Report of Boston Water Board, 1893, p. 85. Report of Massachusetts State Board of Health on Metropolitan Water Supply, 1895, p. 177. *J. Franklin Institute*, **138**, 403.

The second objection is that the standard is not suitable for the measurement of the deeper colors. This is indeed an important question, and had been thoroughly canvassed by the author and his assistants before the publication of the process, and the means for avoiding difficulties from this source were distinctly stated in the article, although the reasons for the precautions to be taken were not perhaps stated as fully as was desirable.

One of the first facts to be learned by persons studying the colors of solutions is that solutions having the same color in one depth or dilution are not necessarily of the same color in greater or less depths or dilutions. The truth of this statement was most strikingly shown in an article published by the author, in connection with Mr. Harry W. Clark[1] in connection with the colors of the various nitrophenols in various dilutions, in which it was shown, for example, that alkaline solutions of ortho- and paranitrophenols are of about the same color when solutions containing one-tenth or a part in a million of nitrogen are seen in depths of 200 mm., while with more dilute solutions the para is more highly colored, and with more concentrated solutions the ortho has the deeper color, and the variations are so astonishingly great that with the most concentrated solutions examined the ortho produced as much color as more than thirty times its weight of paranitrophenol.

The explanation of this remarkable phenomenon has been clearly given by Mr. Desmond FitzGerald and Mr. William E. Foss, in the annual report of the Boston Water Department for 1893.[2] It is there stated that the amount of light which passes through successive equal layers of an absorbing solution diminishes in geometrical progression as the number of layers increases in arithmetical progression; and as the coefficient of transmission varies with different solutions, it often happens that a water matches the standard very closely in hue in a short depth, but appears of quite a different hue in a greater depth. That is to say, taking an extreme case, the coloring-matter in one solution, owing to its chemical or physical properties, absorbs a large percentage of the light from a narrow band of the spectrum,

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[1] *J. Anal. Appl. Chem.*, **5**, 301.

[2] *J. Franklin Institute*, **138**, 401.

while another substance to produce the same apparent color absorbs a small percentage of the light from a broad band in the spectrum. In the first case as the solution is increased in depth or concentration, its color at first rapidly increases until all or nearly all of the rays of light which it is capable of absorbing are exhausted, and further increase in depth effects but little further change in color. In the second case, owing to the smaller percentage absorption of the light rays the color increases to a much higher limit, and in great depths the solution has a much deeper color than is possible in the former case where the action is confined to a narrow band in the spectrum.

A combination of absorption bands having different relative absorptions in the same solution gives rise to the change in hue so often noticed with changing depth or dilution. Thus it is a matter of common experience that a water which is a pure yellow or even greenish when seen in slight depth becomes orange and even quite red when seen in great depths. The way in which these differences occur was well shown by a diagram, in the report mentioned, showing how the standard matching the water at low depth, constantly diverges from it as the depth increases.

There are two possible means of remedying this evil. The first would be to secure a standard in which the coloring-matter was identical in composition with the coloring-matter in the natural waters. Such a standard could obviously be only the natural water standard, which, as shown above, is really no standard, but only a go-between between the waters and the real standards. The other method of avoiding the difficulty is to make comparisons only in such depths that the divergencies between the standards and the waters will not be considerable.

As stated in the report quoted above, the quantity of light transmitted decreases in geometrical progression as the depth increases in arithmetical progression. Let us say that the first cm. of water intercepts one per cent. of those rays of light, whose interception produces the effect of color in the water. The second cm. of water will then intercept one per cent. of the remaining rays, or 0.99 per cent., and the third cm. will intercept one per cent. of the 98.01 per cent. reaching it, or substantially 0.98 per cent., leaving 97.03 per cent. As the color produced is measured by the difference between the light remaining and the full light, we may express the colors produced by one, two, and three cm. of water as, respectively, 1, 1.99, and 2.97. These figures are obviously substantially proportional to the depths; the error of one per cent. in the last case being entirely too small to be taken into consideration. If, however, the process is carried further, the error increases as rapidly as the square of the depth, and at no very remote point becomes important and serious. As an illustration of the substantial correctness of this proposition, the above-mentioned ortho- and paranitrophenols may be mentioned. Notwithstanding the most extraordinary differences between the colors of the comparatively concentrated solutions of these substances, the colors produced by extremely dilute solutions are substantially proportional to the amounts of the respective substances present, and so long as certain limits are not passed, their colors increase at the same rate with increasing depth. The differences between these substances at various dilutions are, however, vastly greater than those between the platinum-cobalt standard and natural waters, and the differences in the latter case with increasing amounts of color are no greater than would be sure to be found with almost any two coloring-matters not of the same chemical composition.

The point to which it is safe to carry the reading of colors is determined by practical experiment and not by theoretical considerations. It was stated by the author in the original paper that up to a point corresponding to colors of 0.9 in a depth of 200 mm. or corresponding lighter or deeper colors in greater or less depths, the variations between the hues of the platinum standard and actual waters were so slight as to be unimportant. In Mr. FitzGerald's report mentioned above, it is stated that colors up to a depth of 1.0 for the same depth can be satisfactorily compared with the platinum standard, this limit being ten per cent. above that suggested by the author, and as long as colors are not measured above these depths the errors introduced are entirely unimportant; and while it is recognized that serious errors might be introduced by the attempt to read much deeper colors, this contingency was distinctly provided against by stating that all waters with deeper colors should be read in a less depth of liquid, or what is practically more convenient, and as far as I have been able to ascertain, equally accurate, the water should be diluted with one, two or more times its volume of distilled water, the color of the diluted water read and multiplied by a proper factor. Mrs. Richards finds it necessary to adopt this same procedure, even with the natural water standards, because, as a matter of fact, the coloring-matters in different waters vary from each other, and the hues produced in different depths also vary in the same way as the hue of the platinum standard varies from that of a water, only in a less degree, and with the natural water standards it is only possible to read accurately colors as high as 2.0, or only twice as high as the limit with the platinum standard.

This dilution of waters with high colors may be objected to on the ground that, a water having, for example, a color of 2.0 does not in reality contain twice as much coloring-matter as a water with a color of 1.0, and that correct results will not be obtained in this way. This is, in fact, the case with the nesslerized ammonia standards and with the natural water standards based upon them, as was shown by the author, who stated that with these standards "color 0.5 is only twice as deep as color 0.2; color 0.8 is only twice as deep as color 0.3; color 1.0 is only twice as deep as color 0.4, etc.;[1] and this very fact is one of the serious objections to the use of these standards. With the platinum standards, on the other hand, the numbers expressing the colors, as nearly as can be determined, are proportional at every point to the actual coloring-matters present, and this simple relation is one of the important practical advantages of the standard.

As a matter of fact, a great majority of the waters, even from swampy regions, have colors low enough to allow accurate direct readings with the platinum standard, and the necessity of diluting the more deeply colored waters occasionally found cannot be regarded as a practical objection to the process. In actual use the convenience of operation, the simplicity of the apparatus required, the accuracy of the work obtained even with unskilled

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[1] American Chemical Journal, 14, 308.

operators, and the permanancy of the standard, even under exceptionally unfavorable conditions, which has far exceeded anything for which we dared to hope when the standard was first used, have abundantly demonstrated its utility; and in view of the ease and accuracy with which it is possible to compare directly the colors of natural waters with metallic solutions, which are, in fact, the only reliable ultimate standards now in use or known, it seems most unfortunate and in every way undesirable to introduce arbitrary go-betweens, not having definite values of their own or capable of being reproduced or controlled except by comparison with other standards.

TECHNICAL ANALYSIS OF ASPHALTUM. No. 2.[1]

BY LAURA A. LINTON.

Received January 3, 1896.

MY former article[2] on this subject has been so favorably received and commented upon that I have been encouraged to offer a second contribution with the object of adding a few more facts to the literature of the subject, as well as to point out certain changes in the method of analysis outlined in the first article, which changes have been suggested by recent analytical work.

The method universally employed for the determination of the incorporated water of asphaltum is that of estimating the loss in weight of the substance when exposed to a temperature of 100° C. The possibility of a loss of more or less of the inherent volatile matter when heated to such a high temperature must have occurred to every one engaged in the analysis of asphaltum. A series of experiments made during the past few months has confirmed my suspicion that such is the case.

The experiment proper consisted in heating a weighed portion of asphaltum in a combustion tube, the general arrangement of the apparatus being the same as that employed in the determination of water in organic analysis. The temperature was gradually raised from the temperature of the room to that of boiling water. The tube was swept out before and after heating with either dried air or dried hydrogen. Simultaneously with

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[1] Read at the Cleveland meeting, December 31, 1895.

[2] This Journal, 16, 809.