Comparison of standard methods for determining the color of water in several countries

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Abstract. Determination of water color is one of the important indicators in assessing water quality. This article compares the available methods used to determine water color according to the international standard ISO 7887 or according to standard methods published by American organizations. The comparison takes into account the specific application of the legislation in the selected countries.

1. Introduction
Natural or anthropogenic influences can affect the color of the water. The color of surface and ground waters is mainly caused by the presence of natural organic substances such as humic matter, especially fulvic acids causing a yellow-brown color of water. In addition to dissolved substances, water may also be colored by suspended substances such as clay or phytoplankton. For this reason, the true color of water, which is caused only by solutes passing through the filter with a pore size of 0.45 µm, is distinguished from the apparent color, which is caused by the color of both dissolved and undissolved substances, usually of a colloidal nature. [1]

There are many standard methods issued by standardizing organizations such as ISO [2], US standards [3], Russian standards (GOST [4, 5], RD [6]) and Chinese standards [7] for determining water color and adoption of these standards may be subsequently regulated by national legislation. Therefore, the methods for determining the color of water may differ in some parameters in different places of world.

2. Examination and determination of color

2.1. Visual examination
According to ISO 7887: 2011, visual determination is a method involving the determination of apparent color by visual observation of a sample in a bottle and represents only the initial information, for example usable in field work. Only an indication of the apparent color determined as soon as possible after sampling should be included in the report. If samples need to be stored, they may be stored for up to 5 days in the dark at 4 ° C ± 2 ° C. Contact of the water sample with air must be avoided during storage, especially if oxidation-reduction reactions leading to color change can be expected. The sample bottle is filled with an unfiltered sample of water, shaken to dissolve any soluble substances and examined in diffused light against a white background. The intensity of colors and shades is recorded. If the sample contains insoluble matter, it shall be allowed to settle before the test. The intensity of coloration (nul, pale, light or dark) and hue (e.g. yellow, yellow-brown) shall be recorded. [2]
This method is adopted from the international ISO standard by the standard of European countries through the CEN/CENELEC organization, the countries currently enabling application of this method are for example Czech Republic, Germany, France and 28 other European countries.

2.2. Determination of the true color using optical instruments
The color intensity of a water sample is characterized by the absorption of light at the wavelength of maximum absorption and is quantified by the absorption coefficient measured by a spectrophotometer. Most yellow-brown colored natural waters and colored samples of treated wastewater discharged from wastewater treatment plants can generally be measured at 436 nm. Treated industrial wastewater does not have sufficiently sharp absorption maxima and these waters must be measured at 436 nm, 525 nm and 620 nm. [2]
Prior to measurement, the interfering effect of undissolved matter present in the water sample is removed by filtration through a membrane filter with a pore size of 0.45 µm. The color of the water depends on the pH value, therefore the pH value should be measured continuously with optical measurement according to ISO 10523 and these results are reported together with other findings. The filtered sample is transferred to a spectrophotometer’s cuvette and the reference cuvette is filled with optically pure water. Natural waters are measured at 436 nm against optically pure water. Further measurements are performed at 525 nm and 620 nm. The spectral absorption coefficient \( \alpha(\lambda) \) is calculated according to following equation:

\[
\alpha(\lambda) = \frac{A}{df}
\]

where
\( A \) is the absorbance of water sample at the wavelength \( \lambda \);
\( d \) is the optical pathlength of the cell (cuvette) in millimetres;
\( f \) is a factor to give the spectral absorption coefficient in reciprocal metres (\( f = 1000 \)). [2]

Like the previous method, this method is adopted from the international ISO standard by CEN/CENELEC organization to European countries and allows usage of this method for example in Czech Republic, Germany, France and 28 other European countries.

2.3. Determination of true color using optical instruments for determination of absorbance using single-wavelength method
The method of determining the true color spectrophotometrically with platinum-cobalt (Pt-Co) solutions as standards is relatively widespread and is described in several standards, but technical implementations differ in some parameters. [2]
The most common ISO standard defines the determination of the intensity of yellow-brown coloration of water by measuring the absorption coefficient at \( \lambda = 410 \text{ nm} \). Comparison with the specific absorption coefficient of a defined calibration solution of potassium hexachloroplatinate and cobalt chloride at the same wavelength allows the determination of color in \( \text{mgl}^{-1} \text{ Pt} \). This procedure is used only for the determination of the true color of samples after filtration through filters with a pore size of 0.45 µm. At the same time as the color determination, the pH of the filtered sample is measured according to ISO 10523. The sample is transferred to the cuvette of a spectrophotometer and measured against a cuvette with optically pure water. The specific absorption coefficient \( a \) of the calibration solution, given as \( A_{410}[\text{mm}^{-1}(\text{mgl}^{-1} \text{ Pt})^{-1}] \), is calculated by the equation:

\[
a = \frac{A_{410}}{100d}
\]

where
\( A_{410} \) is the absorbance of color calibration solution;
100 is the color of the calibration solution in \( \text{mgl}^{-1} \text{ Pt} \);
\( d \) is the optical pathlength of the cell (cuvette) in millimetres. [2]
When calculating and reporting the results of the color intensity of the sample, the volume of water used to dilute the sample must be taken into account. The actual color of water, in $mg/l$ Pt, is calculated according to the equation:

$$C \approx \frac{A_{410}}{ad}$$

(3)

where $A_{410}$ is the absorbance of sample at $\lambda = 410$ nm; $a$ is the specific absorption coefficient of the calibration solution given in reciprocal concentration and millimetres [mm$^{-1}$ $(mg/l$ Pt$)^{-1}$]; $d$ is the optical pathlength of the cell (cuvette) in millimetres. [2]

This method is currently used in countries using ISO standards. In addition to these countries, this method can also be used in the USA, India and Russia. In the USA and India, the current legislation for this method adjusts the wavelength to a value between 450 and 465 nm, according to legislation [3, 8] a good choice is 456 nm. In Russia, there are more changes in technical implementation of this method compared to the ISO standard, as this method is specified in GOST and RD at the same time. [2-6, 8]

The specification of the method described in GOST, as well as in ISO, determines the Pt-Co standard for spectroscopic determination at the 410 nm wavelength. However, the method described in GOST also allows the use of a scale standard using chromium-cobalt (Cr-Co) solutions at 380 nm wavelength. The directive document RD allows the use of both scales of color standard solutions at a wavelength of 440 nm for the determination of true color by optical instruments. [9]

Graduation of the spectroscopic method is also slightly different in these international and state standards. Using ISO standard method only one standard solution ($100 mg/l$ Pt$ - Co$) must be made for the determination of true color. However, US standards need 8 graduation solutions, RD needs 18 and GOST use 11 graduation standard solution for this examination method.

2.4. Visual method for the determination of the color in natural water

Determination of color by visual comparison with hexachloroplatinate standard solutions is described in all examined standards given by legislations. [2-8] The general form of the method of determination is described according to the ISO standard. The method consists in determining the intensity of the yellow-brown color of a water sample by visual comparison with a series of reference solutions. The color is expressed in units of $mg/l Pt$, representing the color intensity of the reference solutions. If the sample is turbid, it shall be filtered with a 0.45 µm pore size membrane filter before color determination. Turbidity caused by clay or other finely dispersed suspended matter cannot be completely removed by filtration. In this case, only the apparent color is determined. [2]

If the color is outside the range covered by the glass standards, you should dilute the sample with a known volume of optically pure water until the color reaches a value within the reference solutions or glass standards. The pH may change during dilution. Therefore, the pH is measured according to ISO 10523 before and after dilution. A series of standard reference tubes is filled to the mark with colored reference solutions. Fill another standard reference tube to the mark with the test sample volume. The reference tube is placed on a white surface which is positioned at such an angle that the light is directed upwards through the column of liquid in the tubes. It is observed with a view from above through the column of liquid. The color intensity of the test sample volume is compared with the standard solutions and the solution closest to the similar intensity is determined. The resulting value of the reference sample closest to the similar intensity, in $mg/l$ Pt. If the sample has been diluted, the original color $C_0$ in $mg/l$ Pt is calculated according to the equation:

$$C_0 = \frac{V_1}{V_0} C_1$$

(4)

where $V_1$ is the volume of the sample after dilution; $V_0$ is the volume of the sample before dilution; $C_1$ is the estimated color of the diluted sample. [2]

The differences in the application of this method of determination by national legislations are not great. China has expanded the color scale of standards. Chinese standard method adds 2 additional matching
solutions in comparison to ISO standard method and extends color scale from 8 to 10 by adding solution with a concentration of 15 and 25 mg l\(^{-1}\) Pt. Meanwhile in Russia is currently possible to use not only the color scale of platinum-cobalt standard solutions as in other countries with this method, but also the color scale of chromium-cobalt standard solutions [4-7].

2.5. Spectrophotometric – Multi - Wavelength Method

The spectrophotometric method using multiple wavelengths can be used to determine the true color in US. The color of a filtered sample is expressed in terms of hue (red, green, yellow, etc.), the degree of brightness and the saturation (pale, pastel, etc.). These values are determined by spectrophotometer using light transmission characteristics of filtered sample. [3]

The method uses 2 samples, one sample with the original pH and species with the pH adjusted to 7 using sulfuric acid and sodium hydroxide to determine the color. A standard pH is necessary because of the variation of color with pH. Both samples are filtered through a membrane filter. Transmittance values (in percent) are determined at least in 10 wavelength ordinates in table 1. The 30 ordinates listed in the US standards can be used for more accurate measurements. The method is measured against a blank sample. [3]

| Table 1. Selected ordinates for spectrophotometric color determinations [3]. |
|---------------------------------|----------------|----------------|
| Ordinate No. | X | Y | Z |
| 1 | 435.5 | 489.5 | 422.2 |
| 2 | 461.2 | 515.2 | 432.0 |
| 3 | 544.3 | 529.8 | 438.6 |
| 4 | 564.1 | 541.4 | 444.4 |
| 5 | 577.4 | 551.8 | 450.1 |
| 6 | 588.7 | 561.9 | 455.9 |
| 7 | 599.6 | 572.5 | 462.0 |
| 8 | 610.9 | 584.8 | 468.7 |
| 9 | 624.2 | 600.8 | 477.7 |
| 10 | 645.9 | 627.3 | 495.2 |

Transmittance values are used for calculation of the trichromatic coefficients x and y from the tristimulus values X, Y, and Z by the following equations:

\[
x = \frac{x}{X+Y+Z}
\]

\[
y = \frac{y}{X+Y+Z}
\]

Localization of point (x, y) on the chromaticity diagrams in figure 1 determine the dominant wavelength (in nm) and the purity (in %). Ranges from table 2 are used to determine sample’s hue. We can notice ranges with a value of ‘c’ referring to the bottom of the diagram used to determine the color characteristics of the sample. The final value of the examination is determined by three characteristics describing the color for the original sample and the pH-adjusted sample. [3]
Figure 1. Chromaticity diagrams [3].

Table 2. Color hues for dominant wavelength ranges [3].

| Wavelength Range | Hue             |
|------------------|-----------------|
| 400-465          | Violet          |
| 465-482          | Blue            |
| 482-497          | Blue-green      |
| 497-530          | Green           |
| 530-575          | Greenish yellow |
| 575-580          | Yellow          |
| 580-587          | Yellowish orange|
| 587-598          | Orange          |
| 598-620          | Orange-red      |
| 620-700          | Red             |
| 400-530c         | Blue-purple     |
| 530c-700         | Red-purple      |

2.6. ADMI Weighted - Ordinate Spectrophotometric Method
As with the previous method, three parameters are used to express the color of the water: hue, chroma, and value. This examination uses the Adams-Nickerson chromatic value formula for uniform color differences. Transmittance is measured by spectrophotometer at multiple wavelengths in the same way as in method described in section 2.5. Transmittance values are converted to a single number that indicates color value. This number is expressed on a scale used by the American Dye Manufacturers Institute (ADMI). [3, 10, 11]
The method of determining the color of water does not differ much in the procedure from the previous method, only the results from the spectrometer measurements are processed and expressed in a different way. The advantage of this method is that it can also be used to determine the color of water outside the Pt-Co standard range. The result of this determination is a trio of color characteristics or ADMI weighted-ordinate values for color [3, 10, 11].

2.7. Multiple dilution method
The method for examining the color of water consists in diluting the sample with optically pure water until the color is barely visible and the diluted sample cannot be recognized in comparison with optically pure water. The color of the diluted sample is observed from top to bottom against a white background. At the same time, the color characteristics of the sample are visually determined, such as: color depth (colorless, light or dark), hue (red, orange, yellow, green, blue, purple, etc.) and transparency of the sample (transparent, cloudy, opaque). The result is expressed in combination with the value of the dilution factor and a textual description of the color properties supplemented by the pH value of the measured sample. [7]

This method is described in Chinese standards only and is currently in use only in China. According to several authors this method is criticized due to the subjective perception of color and the evaluation of the colorless point of the diluted sample. [12, 13]

2.8. Comparison of available methods for determining the color of water

### Table 3.
A summary of available methods for determining the color of water according to applicable legislation in the countries.

| Methods                                      | EU | USA | India | Russia | China |
|----------------------------------------------|----|-----|-------|--------|-------|
| Visual examination                           | ✓  |     |       |        |       |
| Determination of the true color using optical instruments | ✓  |     |       |        |       |
| Determination of absorbance using single-wavelength method | ✓  | ✓   | ✓     | ✓      | ✓     |
| Visual method for the determination of the color in natural water | ✓  | ✓   | ✓     | ✓      | ✓     |
| Spectrophotometric – Multi-Wavelength Method | ✓  | ✓   |       |        |       |
| ADMI Weighted - Ordinate Spectrophotometric Method | ✓  | ✓   |       |        |       |
| Multiple dilution method                     |    |     |       |        | ✓     |

*a 410 nm when Pt-Co color matching solutions, 436 nm when Cr-Co color matching solutions according to GOST; or 440 nm for both color matching scales solutions according RD
*b The alternative Cr-Co scale can be used instead of standard Pt-Co

There are many methods for examination and determining the color of water. List of methods described in this work is summarized in table 3, which shows the possible applications of the method in selected countries.

From the comparison in table 3, it can be seen that China uses only visual methods for water color determination. Methods using spectrophotometry are not mentioned in Chinese standards. According to a comparison of Russian legislative regulations for determining the color of water, the color standards Pt-Co or Cr-Co can be used in Russia, which makes it different from the other countries compared. According to valid legislative documents, in European countries it is possible to use two visual methods to determine the apparent color of water, in addition to a more widespread method of comparing color with colored standards, the Visual Examination method can be used to initially determine the color of water without laboratory equipment, particularly in field work.
3. Conclusion
This article was devoted to a survey of standard methods for determining the color of water in selected countries. Due to the complexity of correct description of measurements according to methods from standards, the methods were described in a brief form omitting technical details and the work mainly focused on comparing the main differences between standard methods and their implementation by national legislatives.

The most widespread methods according to the examined legislative documents are Determination of absorbance using single-wavelength method and Visual method for determination of color in natural water. For the spectrophotometric method, the national standards differed mainly in the wavelength parameter used in the measurement of absorbance. Determination of water color by comparison with color standards differed in the legislation mainly by the prescribed scale for the creation of color matching solutions, other differences were the Russian legislation allowing the use of Cr-Co standards. The biggest difference in determination methods was found in China, where no spectrophotometric methods for determining the true color of water are mentioned.

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4. References
[1] Hangve D and Åkkeson D 1996 Spectrophotometric determination of water colour in Hazen units Wat. Res. Vol 30 (Oslo National Institute of Public Health) pp 2771-2775
[2] ISO EN 7887:2011 2012 Water quality – Examination and determination of colour 3rd Edition (European Committee for Standardization)
[3] Baird R B and A D Eaton et al 2017 APHA Standard Methods for the Examination of Water and Wastewater 23rd Edition (Washington DC American Public Health Association American Water Works Association, Water Environment Federation)
[4] GOST 31868-2012 (Interstate Standard) 2014 Water, Methods for Determination of Colour (Moscow Standartinform)
[5] GOST R 52769-2007 (State Standard) 2010 Water. Methods for Determination of Colour (Moscow Standardiform)
[6] RD 52.24.497-2005, 2005. Directive document of Russian Federation. True color of surface waters. Methods for determination with photometric and visual methods (Russian Federal survey for hydrometeorology and environmental monitoring)
[7] GB/T 11903-89 1989 Water quality - Determination of colority (China State Bureau of Technical Supervision)
[8] IS 3025 Part 4 2021 Methods of Sampling and Test (Physical and Chemical) for Water and Waste Water Part 4 Colour National Standard Body of India (New Delhi: Bureau of Indian Standards)
[9] Zobkov M B and Zobkova M V 2020 New spectroscopic method for true color determination in natural water with high agreement with visual methods Water Research Vol 177 (Russia Northern Water Problems Institute of the Karelian Research Centre of the Russian Academy of Sciences)
[10] McLaren K 1970 The Adams-Nickerson colour-difference formula J.Soc. Dyers Colorists vol 86 (United Kingdom Society of Dyers and Colourists) pp 354-356
[11] Allen W, Prescott W B, Derby R E, Garland C E, Peret J M and Saltzman M 1973 Determination of color of water and wastewater by means of ADMI color values Proc. 28th Ind. Waste Conf. (West Lafayette Purdue University Libraries) pp 661-675
[12] Bao J, Li T and Ren B 2017 Determination of wastewater color by integral spectrophotometry based on complementary color Advances in Engineering Research vol 120 (China Atlantis Press)
[13] Cao P, Zhu Y, Zhao W, Liu, S and Gao H 2019 Chromaticity Measurement Based on the Image Method and Its Application in Water Quality Detection Water vol 11 (Switzerland MDPI)