Photometric Colorimetry

Photometric colorimetry is used in water analytics as well as in industrial production and is usually used to determine quality. In practice, different types of colorimetry have been established.

In the past, “colorimetry” was based on human color vision, which was strongly influenced by individual perception as well as by exterior influences, such as the ambient light and the brightness. Only with the use of photometers and defined and standardized color systems, the subjective visual estimation was replaced with an objective and accurate measurement. This measurement procedure attempts to describe a color using one or more numeric values. Here, different methods can be applied.

Color scales

Some color numbers are calculated using individual or several defined or “standardized” wavelengths. Their basis are reproducibly producible color standards, from which smaller colorations are diluted, stemming from a master solution. Examples for this include e.g. color numbers for iodine, PtCo/APHA/Hazen and Gardner. For some color numbers, such as Pt-Co/APHA/Hazen and iodine, there are no defined calculation bases for photometric measurements. They are exclusively visually defined. The respective standards merely describe that the calculation from the tristimulus values X, Y, Z or the chromaticity coordinates, x, y, z can take place using a defined standard illuminant type and at a normal viewing angle (2° or 10°) according to CIE publication 15:2004. The calculation of these color numbers using spectral photometers is therefore conducted using manufacturer-specific methods that were developed empirically by measuring defined standards.

Other color numbers are converted from the tristimulus values X, Y, Z into three-dimensional color spaces such as CIE-L*a*b* or CIE-L*u*v. The basis for these color spaces is the “standard” color system developed in 1931 by the International Lighting Committee (Commission Internationale de l'Éclairage, CIE).

Water analytics: Spectral absorption coefficient

The spectral absorption coefficient, usually referred to as the SAC, is often used for water analytics in order to photometrically determine the sum of the dissolved organic water content substances. In practice, SAC measurements have become established in two different wavelengths. In the water supply, the SAC is usually used at a wavelength of 436 nm to measure the coloration. The SAC measurement at the wavelength of 254 nm is generally used in the wastewater industry and is used to determine the organic contamination of the wastewater. However, the measurement at 254 nm is a measurement in the ultraviolet (UV) spectrum of the light; therefore it does not represent colorimetry and will not be discussed any more here.

Drinking water should be clear and colorless. Therefore, a measurement of the coloration in the water supply has been established for the qualitative evaluation of the water. Yellow and yellowish brown colorations of drinking water can be caused by iron compounds and humic substances. But, also the influx of fecal matter or physical/chemical contamination can cause a yellow coloration of the water. We generally distinguish between apparent and true coloration. The apparent coloration is caused by dissolved substances and particulate matter of unfiltered samples. Contrary to this, the true coloration is caused exclusively by dissolved substances, the sample must be filtered using a filter featuring a pore size 0.45 µm prior to measuring.

For the determination of the true coloration of the water as per DIN EN ISO 7887, procedure B, measurements of three different wavelengths in visible light are conducted on the filtered water sample at 436 nm, 525 nm, as well as 620 nm, but at least at 436 nm (SAC_{436}). The measured value is standardized to 1 m of optical gap width (Unit: 1/m). Restrictively, it should be noted that the SAC determination can only be made reasonably, if the qualitative composition of the water content substances or the so-called “water matrix” does not change significantly.

Industrial applications

In the industry, colorimetry plays a significant role in the monitoring of products or production processes. On the one hand, the color itself can be a characteristic feature of the product, whose specific limitations must be adhered to. On the other hand, the colorimetry on colorless products can be used to detect quality flaws, which may be caused by contamination and/or aging. Thus, the product is described or evaluated by means of the determined color values. In practice, the most different color measurements are performed, very much depending on the industry.

Hazen/APHA/Pt-Co color number

The Hazen/APHA/Pt-Co color number was originally developed for the measurement of slightly yellow tinted wastewater samples. Today, the Hazen/APHA/Pt-Co color number is mainly used in the chemical or pharmaceutical industries as a quality feature for the evaluation of raw materials, such as greases and oils. The Hazen/APHA/Pt-Co color number is used to detect product aging caused by light and temperature influences, product contamination or process changes. It is only to be used for slightly yellow tinted, nearly clear samples and relates to platinum cobalt standard reference solutions (DIN EN ISO 6271). The DIN standard does not comprise precise measurement directions or a calculation basis. Thus, the measuring method is specific to the manufacturer and it extends from single wavelength measurements at different wavelengths all the way to determinations pursuant to ASTM D5386-05 from the yellowness index as per ASTM E 313, which, however, represents an estimation of Hazen/APHA/Pt-Co color number.

With WTW spectral photometers, the Hazen/APHA/Pt-Co color numbers can be determined at different wavelengths:

- Wavelength 340 nm: Standardization is at 10 mm, cuvette sizes to be used are 10 mm, 20 mm and 50 mm as well as 16 mm round cuvettes.
- Wavelengths 445 nm, 455 nm and 465 nm: Standardization is at 50 mm, and only 50 mm cuvettes may be used.

Yellowness index

The Yellowness index as per ASTM Method E313 is used to detect product changes caused by light, chemical influences and process steps in industrial applications. Here, the deviation between a clear to a more yellowish coloration is determined.

The Yellowness index is calculated as follows:

$$YI = \frac{100\left(C_x X - C_Z Z\right)}{Y}$$

Where X, Y and Z represent the CIE tristimulus values and the coefficients C_x and C_z depend on the viewing angle (2° or 10°) and the type of light used (C or D65).

EBC color number

The European Beer Color or EBC color number (European Brewing Convention) represents an important parameter for the quality monitoring of beer and wort in the brewing process. As per MEBAK 2.13.2, the EBC color number is determined by means of an extinction measurement at 430 nm using 10 mm cuvettes using the following formula:

$EBC = E_{430} * 25 * F$

where E_{430} represents the extinction, measured at the wavelength of 430 nm and F represents the dilution factor of the beer sample.

The beer sample may have to be diluted if the undiluted sample has an extinction value of ≥2.

The typical beer color ranges are, for:

- Light beer 4–15 EBC
- Dark beer 16–35 EBC
- Very dark beer >35 EBC

ASBC color number

The US American beer color ASBC color number (American Society of Brewing Chemists) can be calculated from the EBC color number using the Standard Reference Method (SRM) of the ASBC by applying the following conversion formula:

$$ASBC = EBC / 1.97$$

Gardner color number

The Gardner color number can be used for clear, yellowish brown, liquid samples, such as oil, clear varnish and solutions of fatty acids, polymerized fatty acids, resins, tall oils, tall oil fatty acids, colophon and other products. The calculation from CIE-L*a*b* values as per DIN EN ISO 4630-2 is defined via the CIE standard color value portions x and y.

Sugar color ICUMSA

The sugar colorimetry as per the ICUMSA method GS1/3-7 and method GS2/3-10 can be conducted for solutions of raw sugar, brown sugar and colorized syrups at a pH of 7.0. The calculation is based on the following formula:

$$as = 1000 * \frac{As}{b * c}$$

Where as is the absorption index, As is the extinction measured at the wavelength 420 nm, b is the used layer thickness in cm and c is the sugar concentration in g/ml.

ASTM color scale (mineral oil products)

The ASTM color scale is used for mineral oil products such as lubricants, heating oils, diesel fuels and paraffins. It is defined via the CIE standard color portions X, Y, Z, using the standard illuminant type C and with a standard viewing angle of 2°. The measuring results are standardized to a cuvette size of 32.5 mm.

ADMI color number

The platinum cobalt standard of the American Public Health Association (APHA) was taken over from the American Dye Manufacturers Institute (ADMI).

The ADMI color number is used to measure wastewater and water, whose color intensity corresponds to the platinum cobalt color scale, whose color tone may significantly differ from this.

Iodine color number

The iodine color number is used to determine the color depth of clear liquids, whose color range spans clear to yellowish to dark brown and which therefore is similar to an iodine potassium iodide solution. This iodine color number is used for example, for solvents, softeners, resins, oils and fatty acids.

Color spaces

In 1931, the International Lighting Committee (CIE - Commission Internationale de l'Éclairage) defined the CIE standard color system, or the CIE 1931 XYZ color space in order to correlate the physical causes of the color stimulation and the human color perception. The goal was to express the human color perception in number values in a reproducible and clear manner.

Human color perception takes place via three different color receptor portions in the retina, which perceive red, green or blue. Therefore, the CIE standard color system describes a color via the three standard color values, also referred to as tristimuli, X (red), Y (green) and Z (blue). For the vision pigmentation of three color receptors, the characteristic, wavelength-dependent absorption curves, the so-called standard color matching functions [$X(\lambda)$, $Y(\lambda)$, $Z(\lambda)$] were determined in the range from 360 to 830 nm.

Other important factors for the color perception, besides the receptor, include the light used or the light type, as well as the viewing angle of the observer. The vision angle influences the color perception, as the distribution of the receptors in the eye is not the same. The CIE has defined two different viewing angles, the 2° viewing angle in 1931- and the 10° viewing angle in 1964. Thus, there are the standard spectral value curves for the 10° viewing angle $X_{10}(\lambda)$, $Y_{10}(\lambda)$, $Z_{10}(\lambda)$] (Fig. 1).

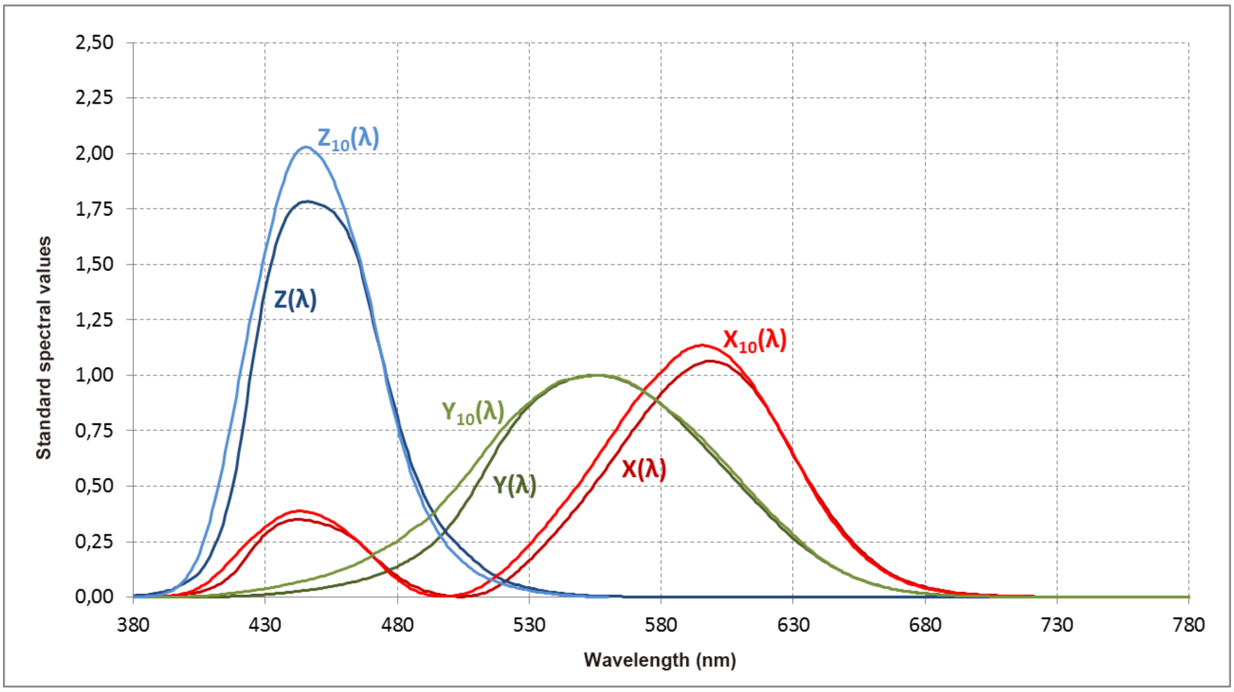

Fig. 1 Standard color matching functions for 2° and 10° observers.

Two different illuminant types were defined in the CIE standard color system, which feature different spectral energy distributions: Illuminant type A represents the light of a 100 W tungsten illuminant light bulb; illuminant type D65 represents daylight. In the meantime, more illuminant types, such as C, D50, D55 or D75 have been added. The relative spectral radiation distribution for the standard illuminant types is also listed in tables. Fig. 2 shows an example of the relative radiation distribution for the illuminant types A and D65.

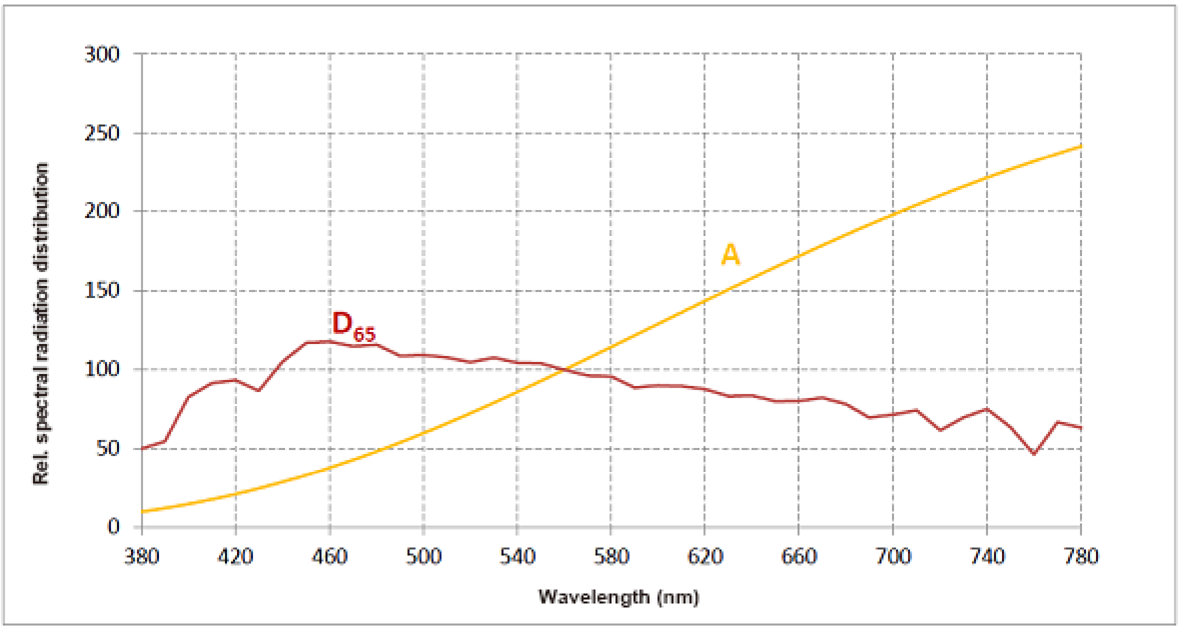

Fig. 2 Relative spectral radiation distribution of the standard illuminants A and D_{65}

For the actual colorimetry, the transmission across the wavelength range from 380 to 780 nm is measured using a spectral photometer. The software uses the table values of the standardized light energy distribution of the set up illuminant type as well as the set up viewing angle to calculate the tristimulus values X, Y and Z or the chromaticity coordinates x, y and z.

If you apply the chromaticity coordinates x and y of the visible spectral colors of the wavelength range from 380 to 780 nm perpendicular to each other, you will receive a curved line. Along with the composition of purple to red, the so-called purple line, this will envelop an area. This enclosed area is the CIE standard color space chromaticity diagram, which, based on its shape is often colloquially referred to as the “horseshoe” (Fig. 3). The pure spectral colors are located on the exterior parable shaped line.

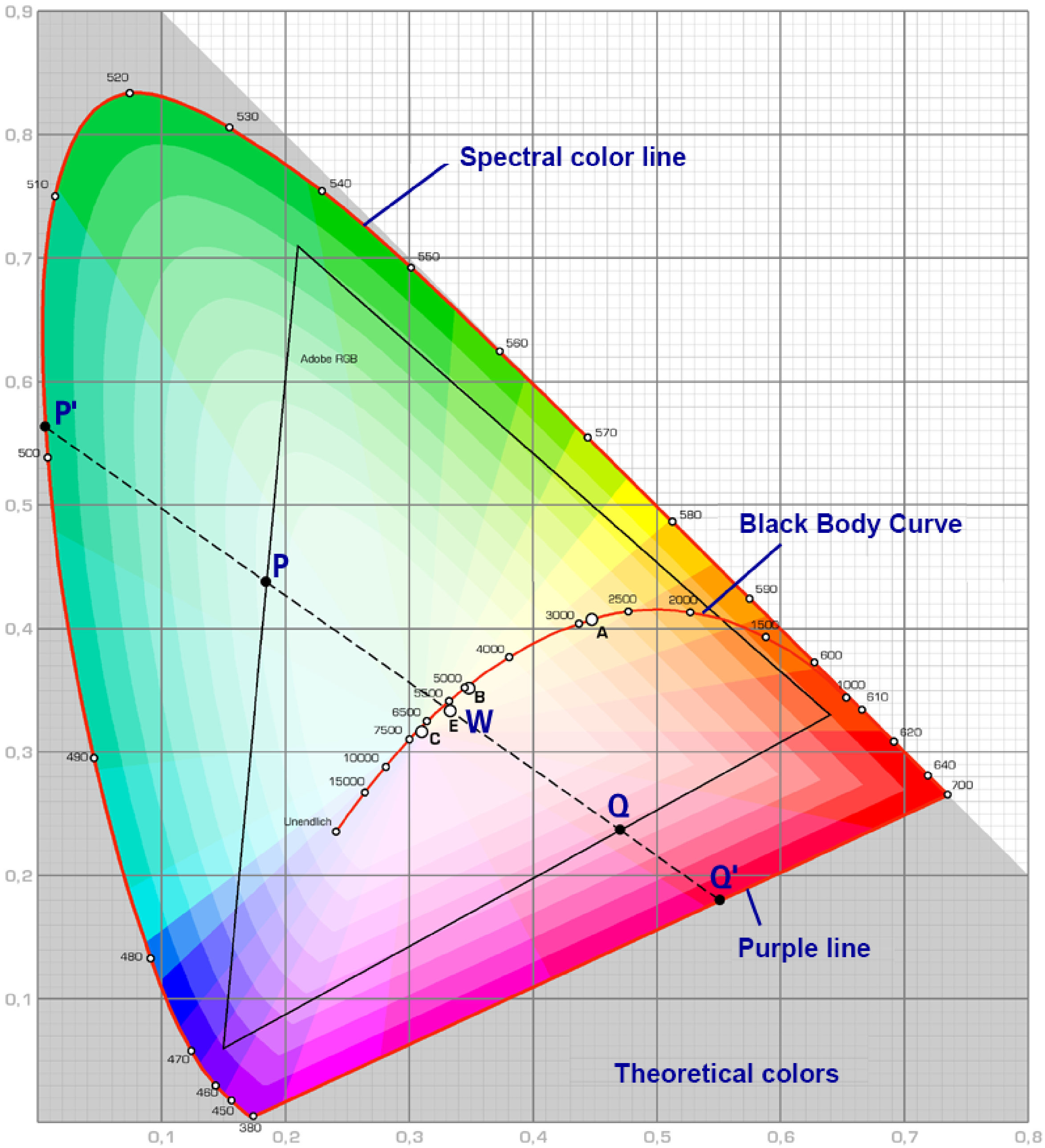

Fig. 3 The CIE standard chromaticity diagram shows all real colors by color tone and color saturation via the chromaticity coordinates x, y. The black triangle in the center represents the Adobe RGB color space. Source: Torge Anders, Wikipedia

The chromaticity coordinates or tristimulus values mathematically precisely reproduce the color perception of the human eye. The disadvantage of these color values is that hardly anybody can imagine a color below these number values. Therefore, they present the basis for the subsequent conversion into different color spaces, which correspond to the color doctrine and are therefore easier to understand.

CIE-L*a*b color space

The CIE-L*a*b is a very frequently used color system. The measured spectral curves are reduced to three coordinates, L, a and b, while the axes of the coordinates are positioned perpendicular to each other (Fig. 4). The L coordinate is standardized to the values between 0 and 100 and describes the brightness of the color, but does not contain any color information. A value of 100 means 100% light (white); a value of 0 means 0% light (black). The coordinates a and b contain the actual color information, they are not standardized and span negative and positive values. The complimentary colors red and green are located on the ac coordinate axis; red is in the positive and green is in the negative range. The more positive or negative the coordinate, the stronger the color green or red. Analog to this, the b coordinate axis represents the complementary colors yellow and blue. If the a or b numeric values equal zero, there is no color, but, depending on the L value, there is a grey tone or white or black.

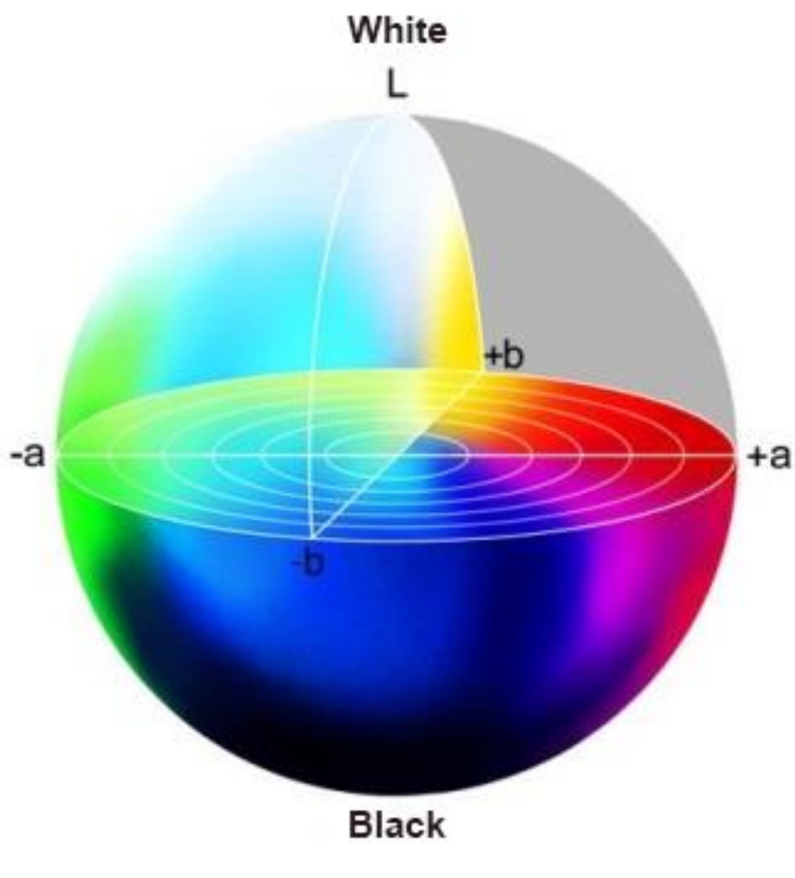

*Fig. 4: Diagram of the three-dimensional CIE-L*a*b color space*

CIE-L*u*v color space

The CIE-L*u*v color space is very similar to the CIE-L*a*b color space described above. The calculation from the CIE tristimulus values is conducted using a different formula in order to reduce the green spectrum and increase the blue spectrum in the presentation. As a whole, you will receive a relatively evenly spaced representation of the color space. The axis of the complementary colors green-red is referred to as u, and the of the yellow-blue is called v.