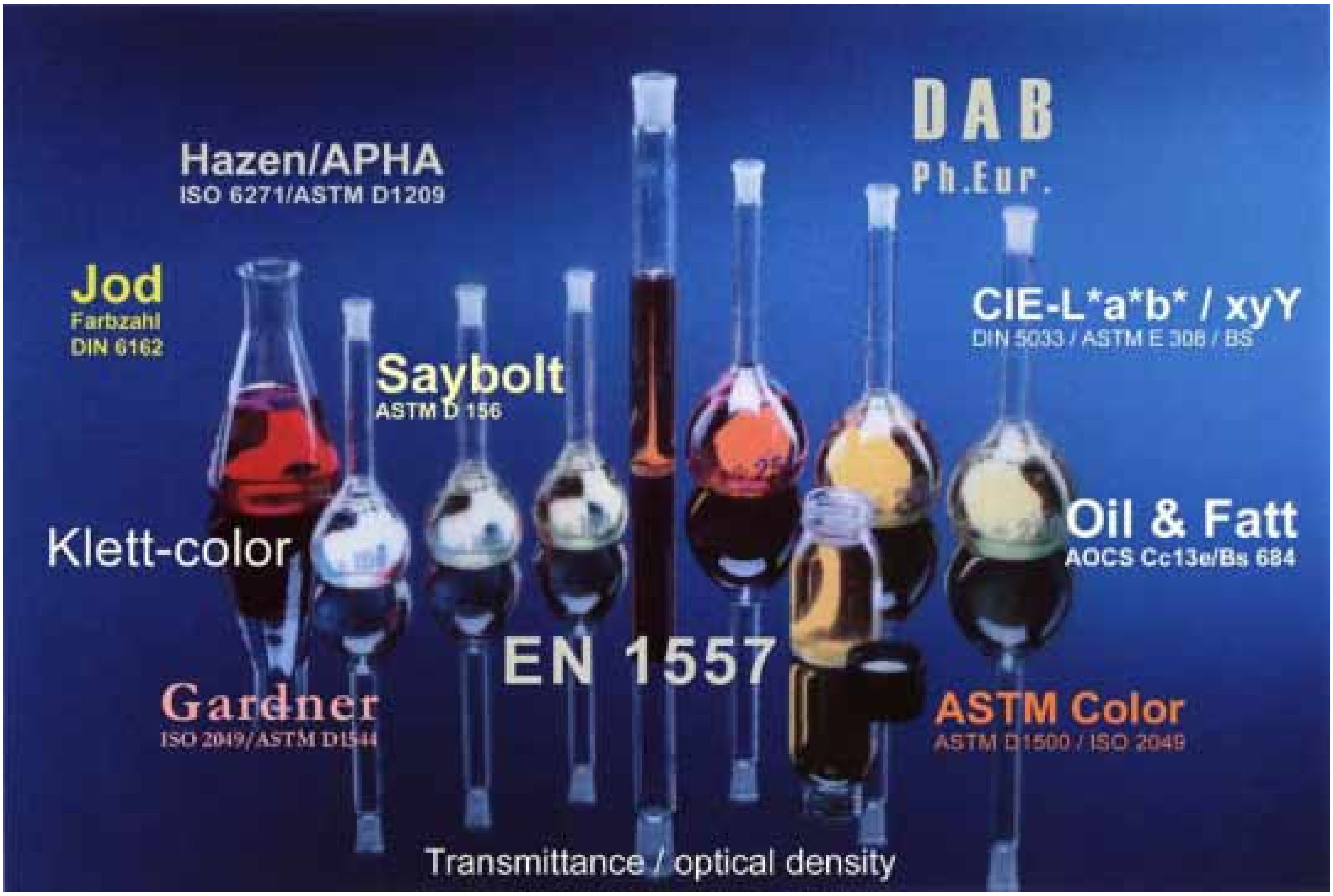
Objective colour assessment and quality control in the chemical, pharmaceutical and cosmetic industries



DR LANGE

Application Report No. 3.8 e

Zusammenfassung

In vielen Bereichen der chemischen Industrie werden die Farbbewertungen z.B. an Tensiden Glycolen, Harzen oder Ölen häufig noch durch visuelle Vergleiche der Produkte mit entsprechenden Farbstandards durchgeführt, obwohl schon im Jahre 1931 durch die DIN 5033 die Basis für eine objektive Farbmessung geschaffen wurde. Die neue EN 1557 definiert jetzt auch die Farbmessung an transparenten Flüssigkeiten als Ersatz für die visuellen Farbbewertungen z.B. mit der Jod-, Hazen- oder Gardner-Farbskala. Die Farbmeßgeräte LICO® 300 und LICO® 100 der Firma Dr. Lange vereinen die objektive Farbmessung nach diesen DIN-Methoden mit der gleichzeitigen, ebenfalls objektiven Messung der herkömmlichen visuellen Farbzahlen.

Summary

In many fields of the chemical industry, especially for tensides, glycols, resins, food stuff, oil and cosmetic products, colour assessment by visual comparison of the product with the relevant colour standards is still going on, although as early as in the year of 1931, DIN-standard 5033 laid down the basis for objective colour measurement. New EN 1557 rule that for transparent liquids colours should be measured instead of being matched visually (e.g. with Iodine DIN 6162, Hazen ISO 6271, Gardner ISO 4630 or Lovibond® -yellow/red values). Colourimeters LICO® 300 and LICO® 100 produced by Dr. Bruno Lange GmbH combine objective colour measurement according to these DIN-methods with another objective measurement of conventional visual colour values.

Résumé

Dans de nombreux domaines de l'industrie cosmétique, l'évaluation des couleurs est toujours effectuée par la comparaison visuelle des produits avec des couleurs types alors que depuis 1931 les bases d'une mesure objective des couleurs furent établies par la DIN 5033. Actuellement la nouvelle EN 1557 définit également l'évaluation de la couleur au moyen de liquides transparents comme substitut des évaluations visuelles des couleurs (ex. iode DIN 6162, Hazen ISO 6271 ou Gardner ISO 4630). Les instruments de mesure des couleurs LICO® 300 et LICO® 100 de la société Dr. Bruno Lange GmbH associent la possibilité d'une évaluation objective des couleurs selon ces méthodes DIN à la mesure visuelle qui est également objective.

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A From visual assessment to objective colour measurement

B The Principles of Objective Colour Measurement

C Instruments to measure the colours of liquids

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A From visual assessment to objective colour measurement

Exacting quality standards and the companies' interest in certification paved the way to colour measurement in the chemical, pharmaceutical and cosmetic industries' daily lab routine. Therefore, suitable measuring procedures must provide objective and traceable production data for documentation which will prove e.g. in case of customer's complaints that given tolerances have been met. Ever constant product characteristics evidence good quality in the opinion of clients and users. Such constancy, however, cannot be maintained by purely subjective assessment in view of nowaday's high demands on quality.

Many different colour systems have been developed for visual colour assessment since the beginning of this century, some of which can still be found among the evaluation criteria of test reports. While industry agreed to a uniform objective method according to DIN 5033[1] and the CIE-Lab-colour system[2] , there is still a large variety of different colour scales like e.g. Iodine, Hazen or APHA, Gardner, FAC or Klett-numbers to describe the colours of liquids. The drawback of these colour scales is the fact that often only some product colours can be clearly assigned to the selected scale. It is often necessary to assess a product once against the Iodine scale, then against Hazen or Gardner scales.

A1 The term "colour"

Every object has individual material qualities or characteristics, for instance volume, extension or density. Colour assessment focusses on the optical characteristics of the material, i.e. its ability to modify incident light waves. If an object is exposed to light, it reflects a certain portion of the light, absorbs another portion and transmits the rest. According to DIN 5036, the relations of these portions to the entire amount of incident light are identified by reflectance ß (reflected portion), transmittance τ (transmitted portion) and absorptance α (absorbed portion), with this equation valid for all media:

$$\beta + \alpha + \tau = 1 \qquad \textbf{(1)}$$

Reflectance ß is the basic value for colour measurement at reflecting materials (surfaces). Transmittance τ is the basic value for colour measurement at transparent materials (clear liquids, foils).

The term "colour" has many different meanings. It is used for the paint which a painter applies to a canvas. It is also used for a characteristic of an object the eye perceives. In the sense of standardisation, "colour" is a sensual perception the human eye transmits to the brain. DIN 5033 sheet 1 defines:

"*Colour is the sensation of a part of the visual field which the eye perceives as having no structure and by which this part can be distinguished alone from another structureless and adjoining region when viewed with just one motionless eye*".

Colour perception is, like any other spatial perception, three-dimensional. This means that colours can be described by three clear measures of quantity like e.g. lightness, hue and saturation, unless verbal descriptions (pink, sky-blue etc.) or, if suitable standards are available, comparative statements like e.g. RAL 9001 or Iodine number 5 are considered satisfactory.

A2 Visual Colour Scales

The still common visual colour systems to assess the colours of transparent liquids were elaborated at the end of the last century. At that time, these colour systems were defined as the first means to match product colours with standard solutions. The parent solutions were made from potassium-platinate, iodine or ferric chloride and diluted to smaller colour gradations. The most common ones beside Iodine, Hazen and Gardner colour values are e.g. the Saybolt-colour number, the mineral oil colour according to ISO 2049 and ASTM D-1500, the Klett-colour number in the cosmetic industry, the FAC[1]-scale, the EBC-scale and the Ph.Eur-colour scale according to the european pharmacopoeia. Moreoever, there are many other colour systems like e.g. Shellac-, Woma[2]-, Dichromate- or Barratt- colour scales.

A2.1 The Iodine Colour Number

DIN 6162 defines the Iodine colour number as mg of iodine per 100ml potassium iodide solution. Colour matching with the Iodine number serves to assess the colour depth of clear liquids like e.g. solvents, plasticizers, resins, oils and fatty acids with colours similar to that of the iodine-potassium-iodide solution at the same path length. For Iodine values around 1 or smaller, it is recommended to use the Hazen colour number according to DIN-ISO 6271. DIN 6162 rules that the iodine colour reference solutions be verified at least once a year by comparison with fresh solutions. As this method is a subjective one, DIN gives no details regarding reproducibility and repeatability. Moreover DIN reads: ″In case of major differences between the sample colour and that of the Iodine colour scale this method should not be employed.″

A2.2 The Hazen Colour Number

The Hazen colour number (ISO 6271, also known as ″APHA[3]-method″ or platinum-cobalt-scale) is defined as mg of platinum per ml solution. To prepare the Hazen parent solution (colour number 500), 1.246g of potassium-hexachloroplatinate (IV) and 1.00 g of cobaltous chloride are dissolved in 100ml of hydrochloric acid and filled-up with distilled water to make 1000ml. The Hazen colour scale is suitable for almost water-clear products. The steps in the light yellowish range are closer than in the Iodine colour scale, reaching water-clear tints. According to ISO-rules regarding storage and shelf-life, the parent solution should be good for one year when stored in a sealed bottle at a dark place. Reference solutions should be prepared freshly.

[1] AOCS Cc 13a-43, FAC Standard Color
[2] White Oil Manufact. Association IP17
[3] American Public Health Association

A2.3 The Gardner Colour Number

The Gardner colour number is defined in DIN ISO 4630. The light yellow Gardner colour numbers (1 to 8) are based on potassium chloroplatinate solutions, numbers 9 to 18 on solutions of ferric chloride, cobaltous chloride and hydrochloric acid. ISO 4630 even approaches colorimetric principles by indicating the chromaticity values x, y and Y for every colour reference solution 1-18 in a table. A considerable drawback of the Gardner scale is the relatively great distance between colour values 8 and 9.

A2.4 The Lovibond®-Colour System

Colour assessment with the Lovibond®[4]-colour system is deeply rooted in the fat and oil industries. The Lovibond®-system can be traced to an English beer brewer who lived in the 19th century: in 1885, he conceived this colour evaluation system to judge his mash. The system was updated with either visual-mechanical or photometric methods of measuring. But visual systems tend to be influenced by subjective factors, and photometric instruments show more or less considerable measuring differences when results are compared directly. Strictly speaking, the employed instrument and the path length of the cuvettes (usually 5¼" (13.34cm) or 1" (2.54cm)) should be specified with the Lovibond®-value. The determination of colour values by LICO® 200/300 is in compliance with the AOCS[5] Cc 13e and BS 684 - 1.14 -methods[13]. The excellent accuracy provided by LICO® 200/300-instruments permits even the use of the 11mm round glass cuvette to measure very small Lovibond®-values. Moreover, LICO® 200 provides for a correction factor to be entered for yellow and red values (Ly and Lr). By modifying these factors, the Lovibond®-values measured with LICO® 200 can be adjusted to present old Lovibond-instruments.

A2.5 The Saybolt- and Mineral Oil Colour Numbers

The Saybolt-scale (ASTM[6] D 156) is employed to match water-clear, colourless to slightly yellowish products (e.g. pharmaceutical white oils, paraffins and mineral oils). The colour gradation of the Saybolt-scale is similar to that of the Hazen-scale (APHA) and is therefore employed for the measurement of water-clear, colourless to slightly yellowish products. The faintest coloration is Saybolt-colour number +30 (corresponding to about 8-9 Hazen), the strongest evaluable Saybolt-coloration value is -16. Saybolt-value 0 corresponds to about 160 Hazen.

The mineral oil colour number (ASTM D 1500) is employed to assess the colours of strongly coloured oils and waxes. Colour numbers 0 to 8 are similar to the Gardner colour scale (colour numbers 0 to 18) regarding their hues and chromas.

[4] Lovibond® is a registered trademark of THE Tintometer® LTD, UK
[5] American Oil Chemists´ Society
[6] American Society for Testing and Materials

A2.6 The European Pharmacopoeia -Colour Number

In the American pharmacopoeia USP 22, chapter <1061> ‘Color-Instrumental Measurement’, colour measurement according to the CIE-L*a*b*-colorimetric system (ASTM Z 58.7.1 and DIN 6174) was defined many years ago. In Europe, however, tests and acceptances in the pharmaceutical industry are still performed by visual colour matching on the basis of the European Pharmacopoeia (Ph Eur). Preparing the colour reference solutions as described in Ph.Eur. is rather laborious and requires utmost care. From three parent solutions for red (cobaltous (II) chloride), yellow (ferrous (III) chloride) and blue colours (cuprous (II) sulphate) and 1% hydrochloric acid, five colour reference solutions for yellow (Y), greenish-yellow (GY), brownish-yellow (BY), brown (B) and red (R) hues are prepared. With these five reference solutions in turn, a total of 37 colour reference solutions is prepared (Y1-Y7, GY1-GY7, BY1-BY7, B1-B9 and R1-R7). Each reference solution is clearly defined in the CIE-Lab colour space e.g. by lightness, hue and chroma.

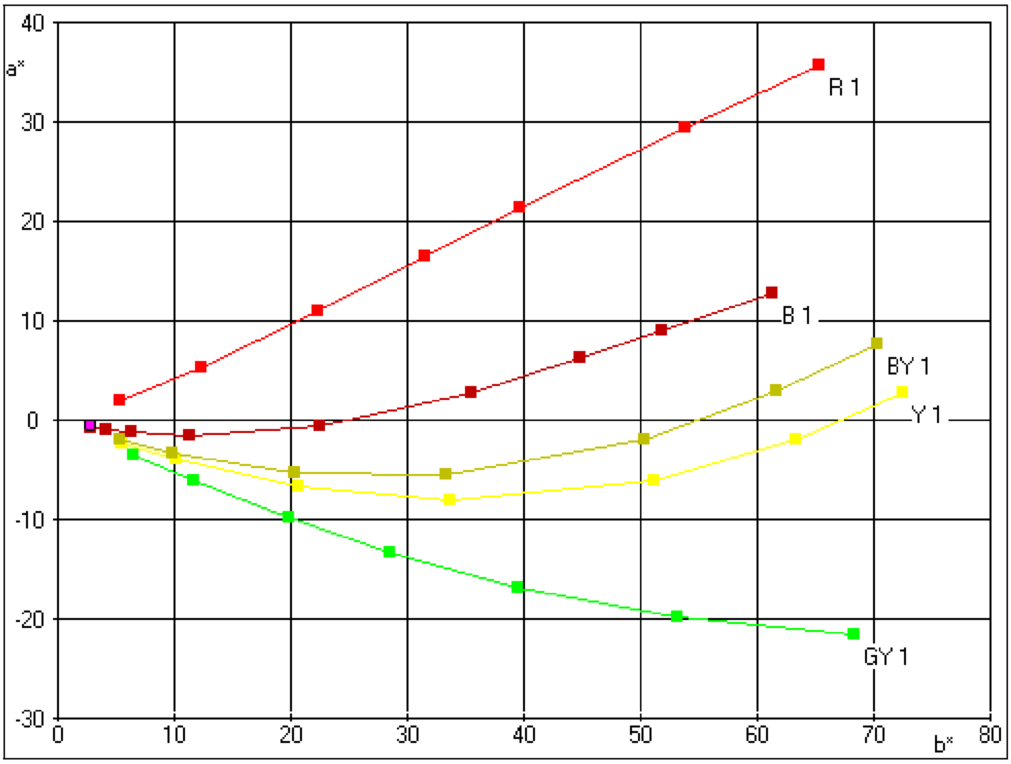


Fig. 1 Ph. Eur.-colour solutions in the CIE-Lab-system

A2.7 The Klett Colour Number

In contrast to the above mentioned colour numbers, the Klett colour number itself is a photometric measure. It is derived from an American Klett-Summerson photometer and is mainly employed for the assessment of raw material in the cosmetic industry. Usually, the Klett-colour number identifies the absorptance of a sample in a square cuvette of 4cm (or 2cm) path length measured through a blue filter (filter no. 42). For these instruments, green and red filters are available, too.

A2.8 The Hess-Ives Colour Number

The Hess-Ives colour number is used in the cosmetic industry for the assessment of fat derivates. It combines the weighted chromas which represent the red, green and blue shares of the transmission spectrum of the measured sample at three wavelengths in one single value. It is defined in the DGK[7]-method no. F 050.2. and LICO® 300 calculates and displays the result according to this method. The Hess-Ives-value is calculated by:

$$H\text{-}I = \frac{(R + G + B) * 6}{\text{layerthickness}} \qquad \textbf{(2)}$$

R, G and B are the colour components for the red (640 nm), green (560nm) and blue (464nm) shares, where R, G and B:

$$R = 43{,}45 * E_{640} \;;\; G = 162{,}38 * E_{560} \;;\; B = 22{,}89 * \frac{E_{460} + E_{470}}{2}$$

A2.9 The Yellowness-Index

Originally, the Yellowness-Index acc. to ASTM D 1925 was a dimension figure used in reflectance colour measurement to describe the yellow cast of a reflecting surface (e.g. plastic, paper). The new ASTM D 5386-93b [11] now defines the Yellowness-Index also for transparent liquids on the basis of CIE XYZ-tristimulus values, standard illuminant C and the 2°-standard observer (see EN 1557).

$$Yi = 100 * \frac{Tx - Tz}{Ty} \qquad \textbf{(3)}$$

[7] Deutsche Gesellschaft für wissenschaftliche und angewandte Kosmetik

B The Principles of Objective Colour Measurement

As early as in 1931, the colorimetric principles were laid down on an international level by standardising light sources, a standard observer and a colour identification system known as CIE[8]-colour system. To understand terms and abbreviations like e.g. C/2° or D_{65} and to employ the CIE-colour system correctly, the following definitions must be known.

Figure 2 shows three basic colour perceptions:

a) reflexion

b) transmission

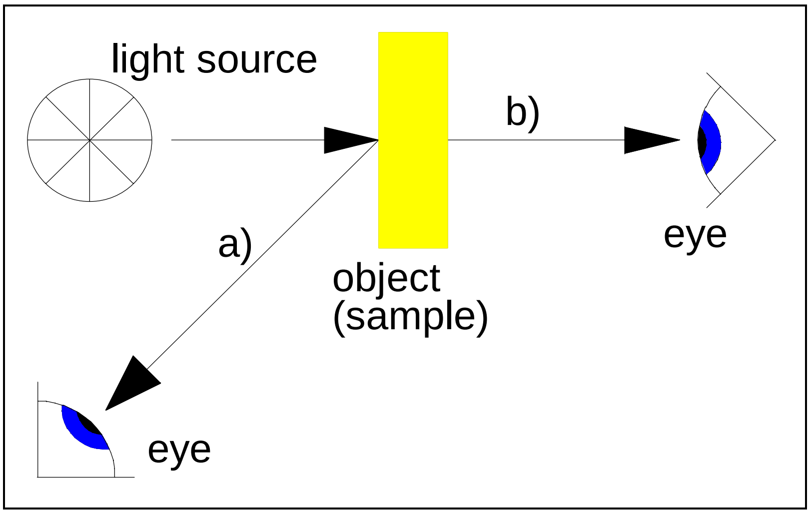


Fig. 2: Colour perceptions

Colour assessment by reflexion (a) is used for solid, opaque products like e.g. plastic parts, painted surfaces, textiles or also printed packings. In today's practice, colorimeters featuring measuring geometries 45°/0° or diffuse/8° are employed.

The colours of liquid and transparent products or raw materials like e.g. resins, tensides, oils, fatty acids, detergents, glycols and glycerines are usually determined by transmission (b).

As shown in figure 2, pigment colours can only be determined when there is a light source, an object and an observer. To make colour assessment objective, the surrounding factors like „light source, observer and optical set-up“ must be defined in a corresponding standard.

[8] Commission Internationale de l'Eclairage

B1 The human eye

The human eye is a highly sensitive sense organ capable of discerning about one million colour hues and detecting even the slightest deviation in direct comparison of reference and sample colours.

For visual colour assessment, however, the eye is reliable only to a certain extent, because changing ambient conditions and the mood of the observer are easy to influence.

What is more, about 8% of males and 0.5% of females have an abnormal colour vision, which may lead to wrong colour assessment.

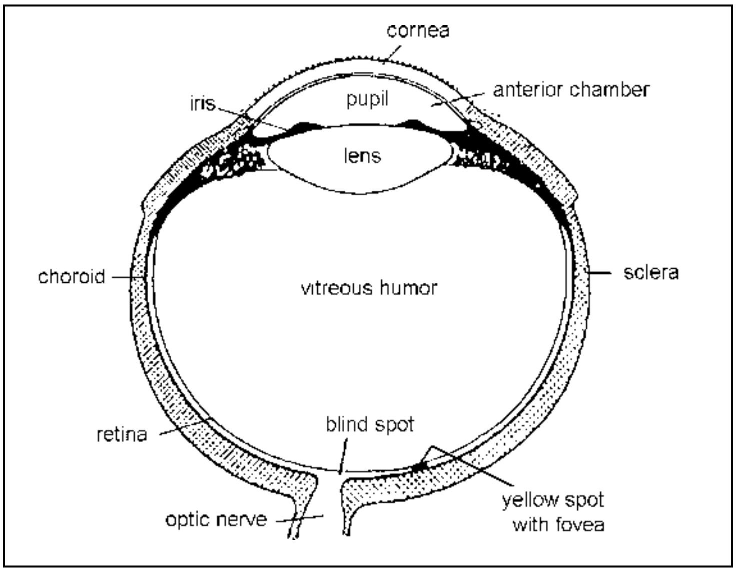


Fig. 3: Structure of the human eye

The retina of the human eye (Fig. 4) contains light-sensitive cones for daytime colour vision (light-adapted eye) and so-called rods for night-vision (dark-adapted eye).

The cones are subdivided into red, green and blue sensitive ones. The rods have no influence on colour vision. They receive only light/dark signals.

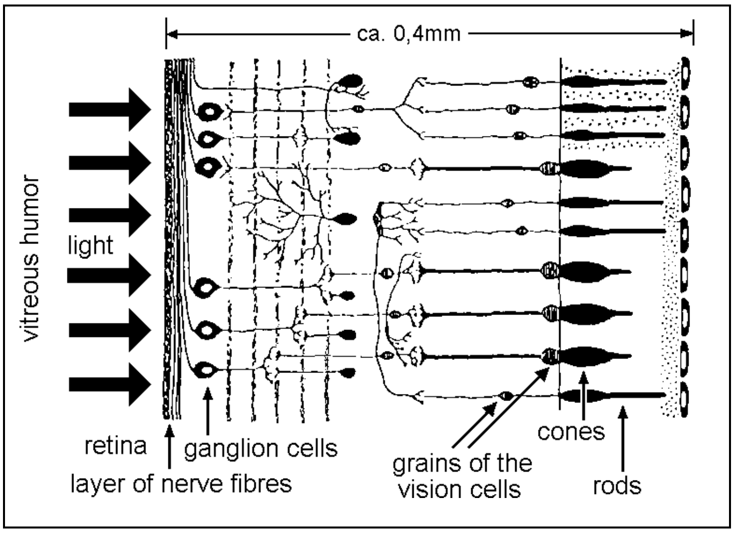


Fig. 4: The retina

DIN 5033 part 3 defines the spectral colour sensitivities of the three cone types for a light-adapted eye (i.e. for daytime colour vision with the cones). In this connection, the term of "colorimetric standard observer" is employed. The spectral sensitivities of the cones are termed standard spectral functions (fig. 5) and stated in numbers as x(λ), y(λ) and z (λ), where λ is the wavelength. But the statistical distribution of rods and cones over the retina is not even. In the centre, i.e. opposite the pupil, there are only colour sensitive cones which are gradually replaced towards the outside by rods.

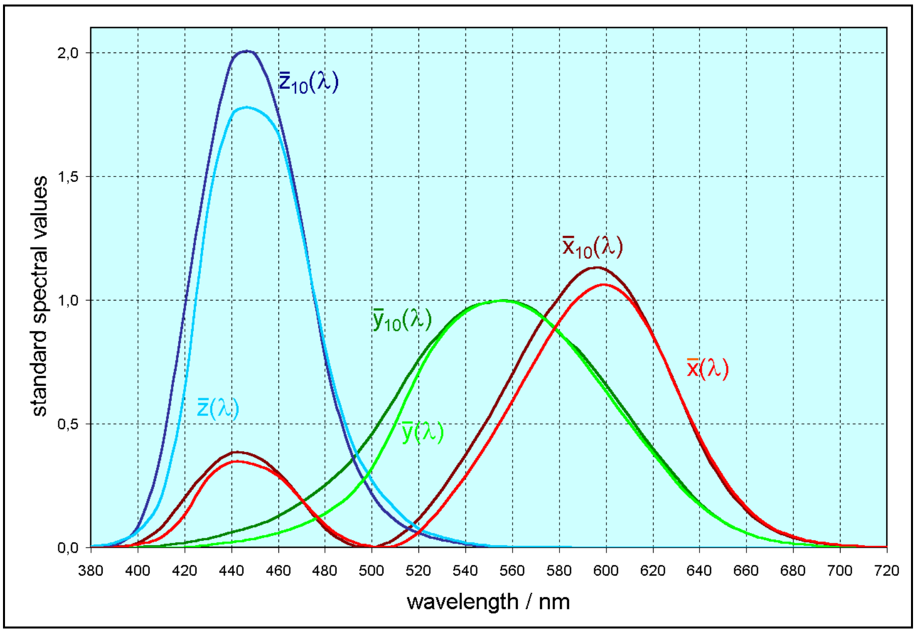


Fig. 5: CIE colour matching functions x(λ), y(λ) and z(λ)

Therefore, colour perception (or colour stimulus) changes with the size of the surface to be assessed. Owing to this change in the colour stimulus when observing coloured surfaces of different sizes, DIN 5033 defined a 2°-standard observer standard observerin 1931 and a 10°-standard observer in 1964. The 2°-standard observer evaluates a coin-size coloured surface at a distance of 50cm, whereas the 10°-standard observer evaluates a postcard-size surface at the same distance. To differentiate between the measurings of the 2° and 10°-observers, the 10°-values are marked with an index (10).

B2 The influence of light on colour perception

The eye perceives only a small part of the electromagnetic radiation at wavelengths between 380 nm and 720 nm (nm = nanometer = 10^{-9}m).

The spectral characteristic and colour temperature of the light source play an important role in the assessment of colours, too. A red, yellow or blue light source is useless for colour assessment because it emits only a part of the perceptible radiation which makes the illuminated sample reflect only this part in turn.

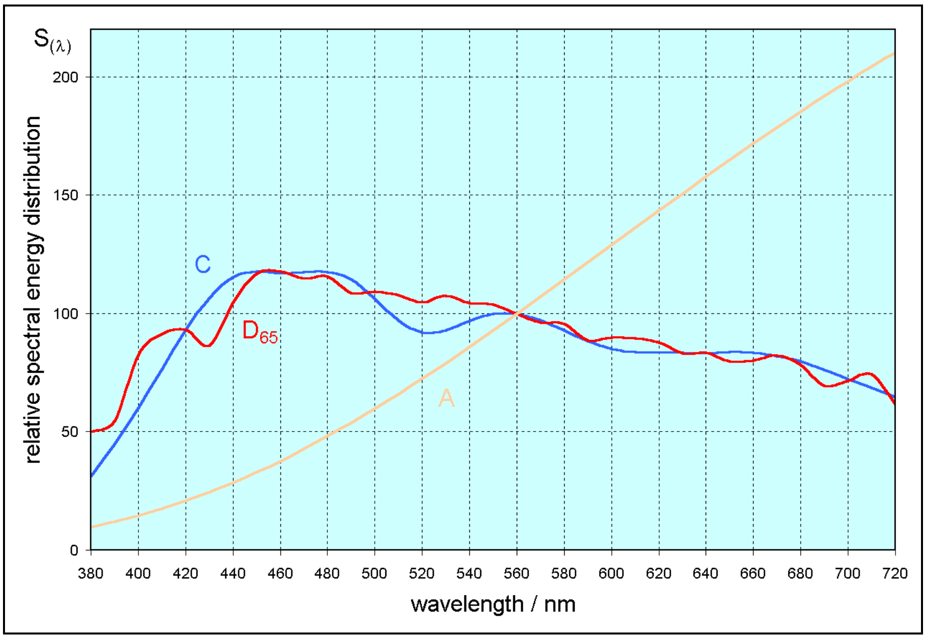


Fig. 6: Standard illuminants A, C and D_{65}

The colour temperature influences the whiteness of the light source. Standard illuminant A was defined as early as in 1931 and corresponds to the spectral function of a 100W tungsten lamp emitting a colour temperature of approx. 2800 Kelvin. Standard illuminant C has a colour temperature of 5600 Kelvin, standard illuminant D_{65} 6500 Kelvin. The main difference between standard illuminant C and D_{65} is the fact that in the near UV-range (300 to 400nm) the latter has a ultra-violet radiation intensity similar to natural sunlight.

The relative spectral power distributions S(λ) for the standard illuminants A, C and D_{65} are defined by part 7 of DIN 5033 (Fig. 6, Standard illuminants A, C and D_{65}).

B3 Methods of colour measurement

Basically there are three different methods to assess colours in the lab:

- visual colour matching
- tristimulus method
- spectral method

B3.1 Visual colour matching

Visual colour matching means to compare sample and reference colours by eye. In fact, this procedure is no measurement and cannot provide objective results. It is mainly employed for transparent liquids where the product is compared with reference solutions (like Iodine, Hazen or Gardner colour standards). Nevertheless, these liquid standards are colourfast only for a limited period, i.e. they change hue by the influence of light and must be replaced after six months at the latest, depending on how they are stored. The only alternative to liquid standards were additional devices, the so-called comparators, permitting visual colour matching of the samples using coloured glass or colour dots. The main disadvantages of visual colour matching are, among others, the subjective factors (abnormal colour vision of the colour matcher or bad and unsteady illumination) and the difficult assessment of hue deviations by red or green stains between sample and reference. It is true that standard regulations explicitly prevent the latter case by stating that only products similar in hue to the reference solution may be evaluated by these methods, but in practice, this instruction is often not observed, because the term "similar" leaves room for interpretation.

B3.2 The tristimulus method

In the tristimulus method, the light beam transmitted by the sample is dispersed into its red, green and blue proportions after passing through colour filters adapted to the colour sensitivity of the eye and the resulting intensity is measured by photoreceptors. A reference beam path makes sure that disturbances by e.g. lamp or temperature drifts are compensated.

The measured signal indicates transmittances Tx, Ty or Tz, depending on the colour filter employed (X, Y or Z).

From these transmittances, the standard tristimulus values can be determined by equations (4) to (6).

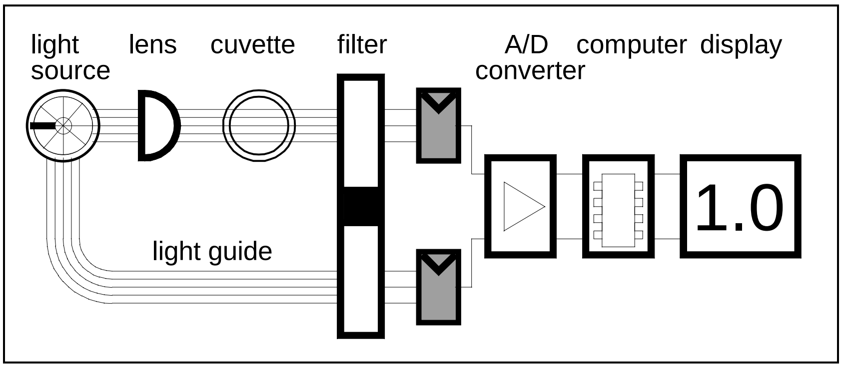


Fig. 7: Beam path in LICO® 100

$$X = a * Tx + b * Tz \qquad (4)$$

$$Y = Ty \qquad (5)$$

$$Z = c * Tz \qquad (6)$$

As factors a, b and c depend on illuminant and observer, they must be put in correspondingly.

B3.3 The spectral method

In the spectral method, light is dispersed into its spectral proportions with a concave grid and the transmittance $\tau(\lambda)$ of the sample is measured at intervals of 10nm.

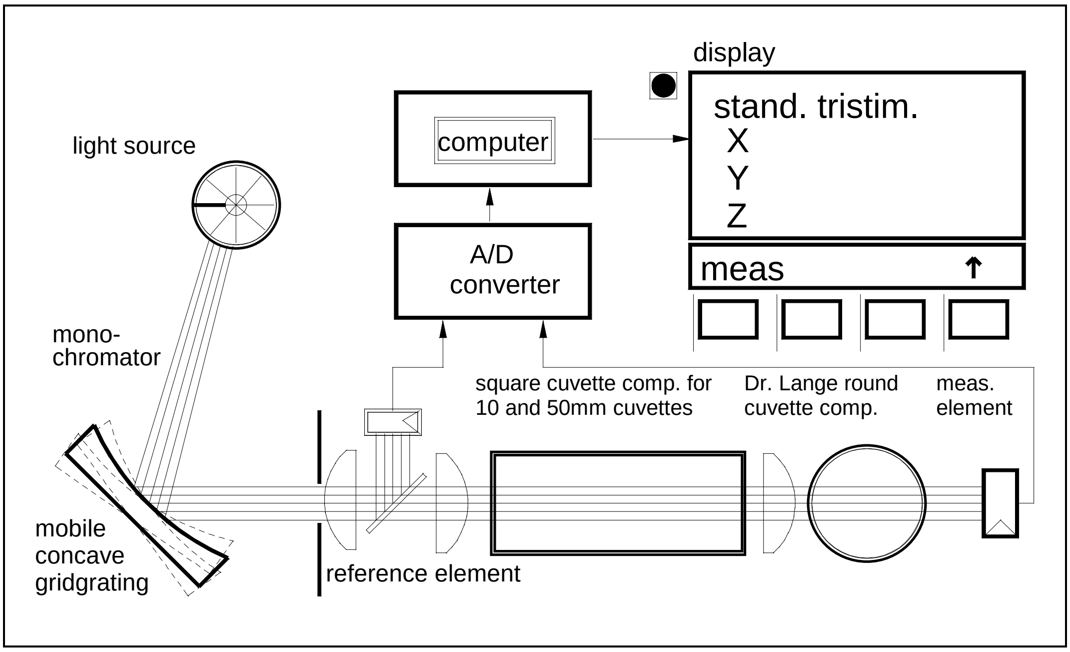


Fig. 8: Measuring principle of LICO® 300/200

Standard tristimulus values X, Y and Z are calculated from the chosen standard illuminant S(λ), standard spectral functions x(λ), y(λ) and z(λ) and the transmittances τ(λ) by equations (7) to (9) (see DIN 5033 part 4).

$$X = k * \int_{\lambda=380}^{720} S(\lambda) * \bar{x}(\lambda) * \tau(\lambda)\, d\lambda \quad \textbf{(7)}$$

$$Y = k * \int_{\lambda=380}^{720} S(\lambda) * \bar{y}(\lambda) * \tau(\lambda)\, d\lambda \quad \textbf{(8)}$$

$$Z = k * \int_{\lambda=380}^{720} S(\lambda) * \bar{z}(\lambda) * \tau(\lambda)\, d\lambda \quad \textbf{(9)}$$

Factor k (equation (10)) serves to standardize tristimulus value Y for perfect white (τ(λ)=1). Therefore, tristimulus value Yn is always 100 for all combinations of standard illuminants and standard observers.

In practice, the infinitely small intervals dλ are converted into limited intervals Δλ (usually 10nm) and integrals (7) to (9) are converted into summation equations.

$$k = \frac{100}{\int_{\lambda=380}^{720} S(\lambda) * \bar{y}(\lambda) * d\lambda} \quad \textbf{(10)}$$

Standard tristimulus values X, Y and Z are the fundamentals of colorimetry. But they alone do not give any direct information on lightness, hue or chroma of a colour. Therefore, they are transformed to other colorimetric systems.

B4 Colorimetry and standard colour systems

Colorimetry is employed to determine transmittances T_{380} to T_{720} (spectral method) or transmittances Tx, Ty and Tz (tristimulus or filter method). When these values are known, the colour itself is measured. Just like geometry describes the relation of a point within a three-dimensional cartesian system, colorimetry describes a spectrum locus within the colour space of real colours. Standard tristimulus values X, Y and Z are calculated by the a.m. equations as shown in the examples. They are the fundamentals of colorimetry. As standard tristimulus values X, Y and Z form no rectangular coordinate system (triangle coordinate) and give no direct information about lightness, hue and chroma of a sample, they are transformed to other (rectangular) colour systems for better understanding and graphical representation. By and by, several theories on human colour perception were introduced and dozens of colour systems developed. We will confine ourselves to show just the most important ones for practical use. DIN 5033 part 3 defines the tristimulus system and the L*a*b*-colour space CIE 1976.

B4.1 The tristimulus system

Chromaticity coordinates x and y (say: small x and small y) in the tristimulus system are calculated from the standard tristimulus values X, Y and Z by the following equation:

$$x = \frac{X}{X+Y+Z} \quad \textbf{(11)} \qquad\qquad y = \frac{Y}{X+Y+Z} \quad \textbf{(12)}$$

If you mark chromaticity coordinates x and y for all real body colours in a diagram, you receive a solid bounded by the loci of the spectral colours (Fig. 9). One level of the colour space shows only colours of equal lightness. The loci of colours differing in lightness will therefore lie on different levels. In practice, however, colours of different lightness are marked on the same level of a colour chart with the numeric lightness values. A graphic display including lightness, hue and saturation of a trichromatic stimulus calls for a spacial representation (Fig. 10).

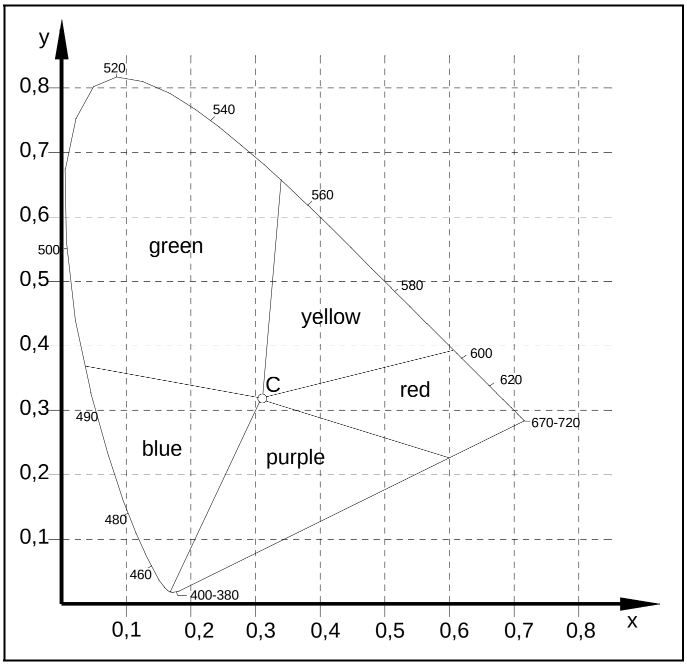


Fig. 9: Chromaticity diagram of the tristimulus system-

The third axis is in vertical position toward the xy-plane and is calculated by the tristimulus value Y. The colour solid is bounded by the pure spectral colours. The loci of all real colours lie within the colour solid. As a rule, the standard observer used for measuring or calculating must be taken into account for any graphic representation, because graph and spectrum location of the light source differ for 2° and 10° standard observers.

A more telling representation than the tristimulus system is the L*a*b*-colour space (Fig. 11).

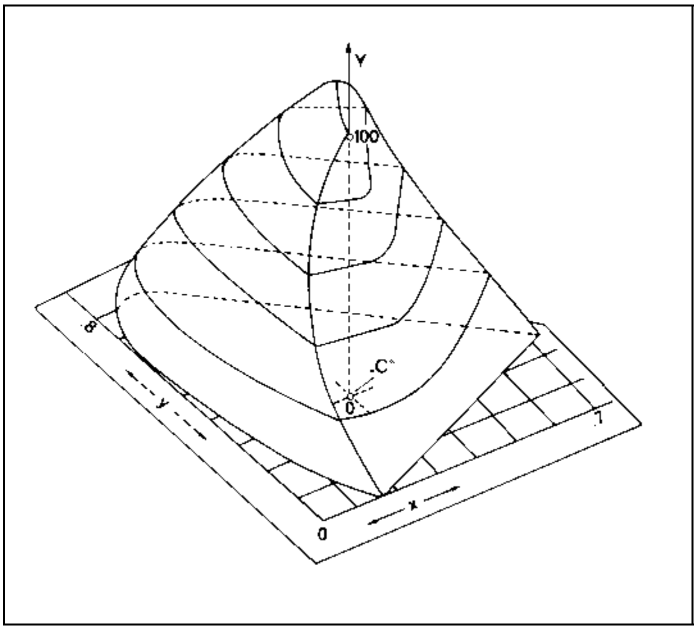


Fig. 10: Three-dimensional colour space with Y-axis

B4.2 The CIE-L*a*b*-system

The CIE[9]-L*a*b*-system (DIN 6174 [2], among others) is in better harmony with subjective colour vision.

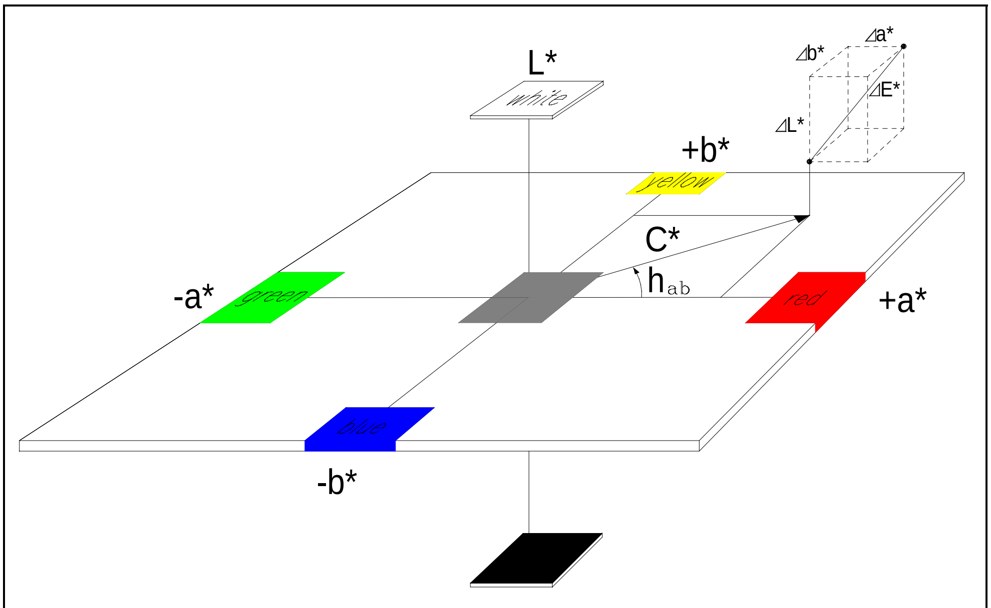


Fig. 11: CIE-L*a*b*-System (DIN 6174)

The L*-axis gives the lightness of a colour, the a*-axis the red-green and the b*-axis the yellow-blue share. The L*-values are always positive and lie between 0 for ideal black colours and 100 for ideal white ones. Red hues have positive a*-values, green ones negative a*-values accordingly. Yellow hues have positive b*-values, blue ones have negative b*-values. Colour loci distributed in a circle around the L*-axis have the same C* (chroma), but different h (hue). Colour loci lying on a radius beam starting from the L*-axis are equal in hue h, but of increasing chroma. The angle between radius beam and the positive a*-axis is defined as hue h_{ab}, stated in angular degrees between 0° and 360° and counted in mathematically positive sense (anticlockwise).

[9] Commission Internationale de l'Eclairage

The CIE- L*a*b*-values are calculated from the standard tristimulus values by equations (13) to (17) and therefore depend on the employed illuminant (A, C or D_{65}) and standard observer (2° or 10°), too.

$$L^* = 116 * \sqrt[3]{\frac{Y}{Y_n}} - 16 \qquad \textbf{(13)}$$

$$a^* = 500 * \left(\sqrt[3]{\frac{X}{X_n}} - \sqrt[3]{\frac{Y}{Y_n}} \right) \qquad \textbf{(14)}$$

$$b^* = 200 * \left(\sqrt[3]{\frac{Y}{Y_n}} - \sqrt[3]{\frac{Z}{Z_n}} \right) \qquad \textbf{(15)}$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \qquad \textbf{(16)}$$

$$h_{ab} = \arctan\frac{b^*}{a^*} \qquad \textbf{(17)}$$

B4.3 The Hunter-Lab-system

The Hunter-Lab-colour scale has been used for the assessment of surface colours since 1960, mostly in the USA. It is similar to the CIE-L*a*b*-scale (L = lightness, a = red-green-axis, b = yellow-blue-axis). The Hunter-Lab-colour values, just like the CIE-L*a*b*-values, are calculated from standard tristimulus values X, Y and Z, but with other equations and, therefore, other colour values. We integrated this colorimetric system in LICO®, because the food and drinks industries continue (or start again) to use Hunter-Lab-values if measuring data is to be exchanged with American companies.

B5 New EN 1557

On the basis of DIN 5033, the new EN 1557[3] also define colour measurement at transparent liquids to replace conventional visual colour scales[17]. For this measurement, transmittances X, Y and Z of a sample are determined for 10mm path length. The calculation of colour values according to this standard is referred to standard illuminant C and 2°-observer.

Scope and purpose of these standards

These standards describe a photometric procedure to objectively assess optically clear, slightly coloured transparent liquids by measuring the ″pure transmittances″. This procedure determines all standard tristimulus values according to DIN 5033, parts 2,3 as well as e.g. Iodine, Hazen and Gardner colour numbers in an objective way.

Procedure in short

Calibrate a suitable photometer using e.g. 1cm square cuvettes with a cuvette containing distilled water to Tn = 100.0 (n = X, Y and/or Z). Then fill the clear liquid sample into a cuvette of the same type and measure. You may also use cuvettes of other path lengths than 1cm (e.g. 5cm cuvettes to measure almost water-clear samples). Dr. Lange supplies cuvettes of all usual path lengths and materials (especially disposable 50mm cuvettes made of very resistant PMMA-plastics).

Sample preparation and measurement

Fill the optically clear liquid into a cuvette, avoiding bubbles. Warm up pastes or solid products (e.g. with a Dr. Lange thermostat). Eliminate turbidities in liquids by filtration. Put a cuvette with distilled water into the photometer compartment and calibrate to 100. Then put a cuvette with the sample into the compartment and measure transmittances.

Evaluation

The transmittances determined can either be used directly (e.g. for production control) or transformed to other CIE-colour values.

Test Report

The test report should specify:

a) identification and type of sample
b) transmittances Tx, Ty and Tz
c) deviations from path lengths, illuminant C and 2°-observer
d) test date.

The advantages of an all-European objective colorimetry are obvious. The exact colour identification by colour stimulus measurement enables clear statements of colour values where conventional visual methods fail because sample and reference differ in hue.

Fig. 12 compares the EN 1557-standardized transmittance Tz and the visual colour scales e.g. Iodine, Hazen, Gardner and Lovibond referred to a cuvette path length of 10mm. The comparison of visual colour systems lacks precision owing to hue difference between the systems. The representation in Fig. 12 is just supposed to give a general idea.

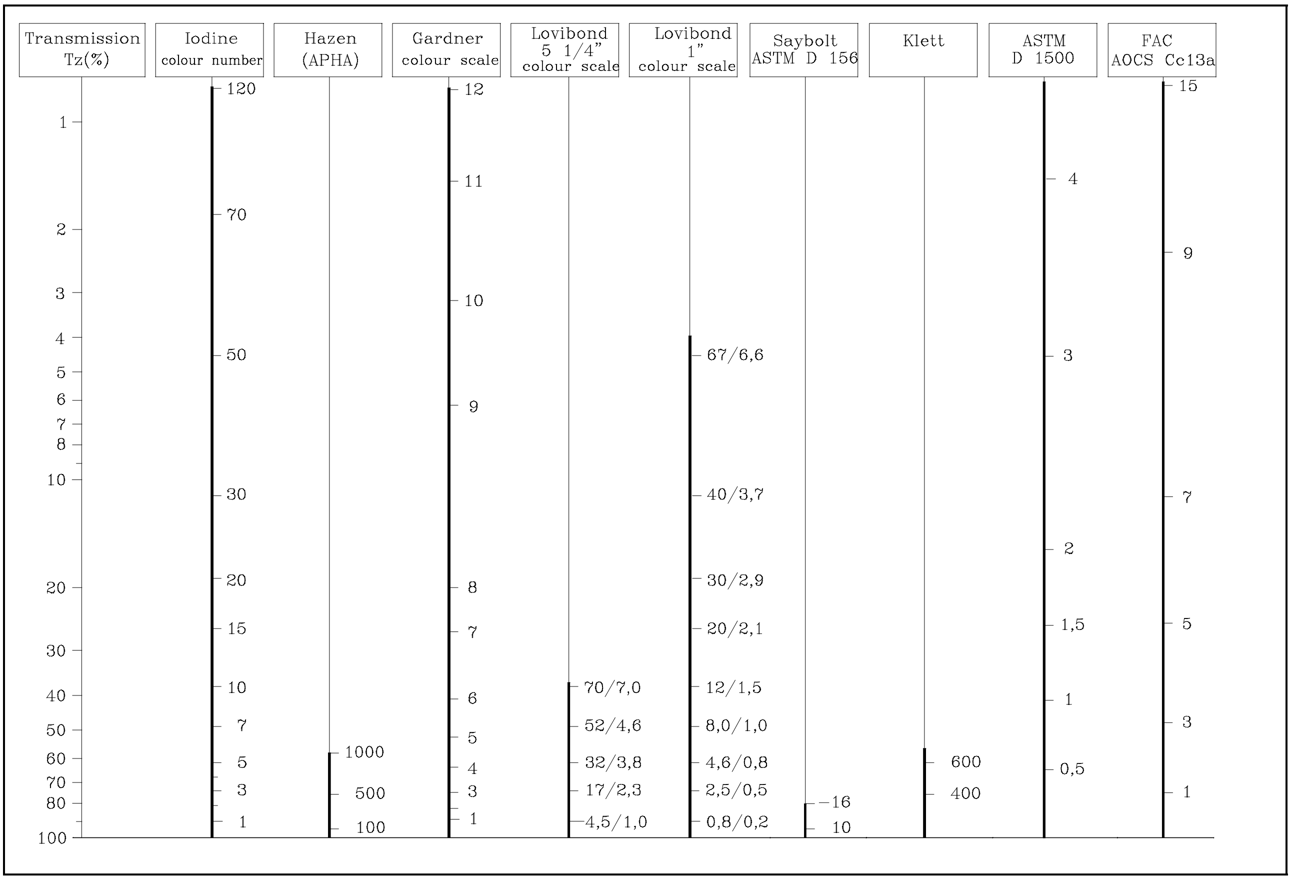


Fig. 12: Comparison of visual colour systems with the Z-transmittsance

Fig. 13 shows the colour graphs of the Iodine, Hazen (APHA) and Gardner scales in the CIE-Lab-colour space referred to a cuvette path length of 10mm.

The hue differences between the scales are evident here.

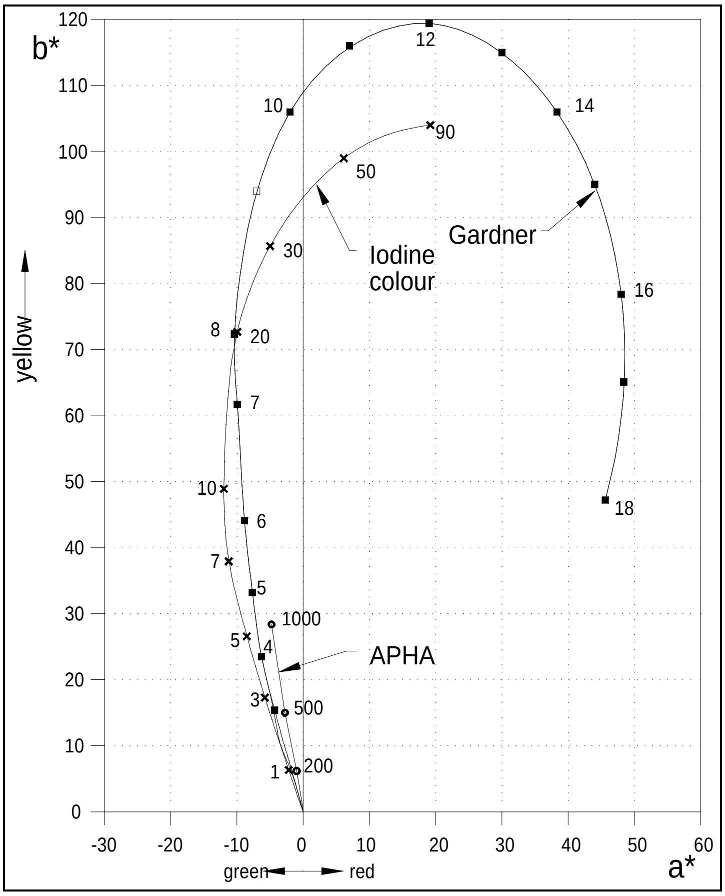
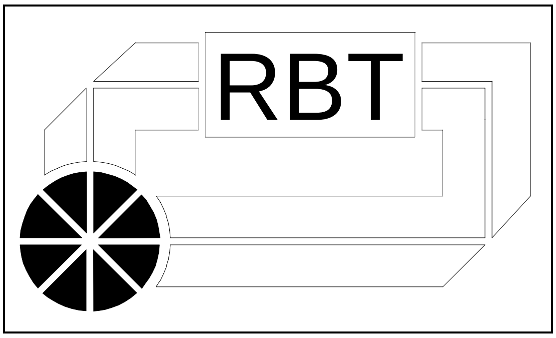


Fig. 13: Iodine-, Hazen- and Gardner-colour scales in CIE-Lab-colour space

C Instruments to measure the colours of liquids

Dr. Lange colorimeters are high-quality optical instruments using perfected and well-proven technologies. Thanks to their very simple handling and universal application, they are the best choice for routine checks at the goods receipt department, in production and quality control. All instruments feature a modern optical system with reference beam path (RBT-technology) to automatically compensate disturbances cause by e.g. lamp aging or temperature changes.



C1 The LICO® 300

The LICO® 300 is a spectral colorimeter which has been specially designed to evaluate the colour numbers and measure the colours of transparent liquids in conformity with EN 1557. LICO® 300 is the new benchmark for top reliability and unique operator friendliness through menu-controlled user guidance on the large graphic display and fully automatic measurement. It functions in accordance with the described method with standard light type C and 2° standard observers.

The LICO® 300 can be used for quality control and production control in almost all areas of the chemical, cosmetic and pharmaceutical industries, e.g. for assessing surfactants, oils, fats, resins and synthetic resins or pharmaceutical active substances.

Fig. 14: LICO® 300

LICO® 300-Features

- Automatic cuvette detection
- Backlit graphical display
- 4 User profiles with password protection
- GLP-conformable print-out
- Integrated test media control
- Program module

It replaces conventional visual colour assessment by fast and objective colour measurement. For Hazen colour evaluation of water-white liquids in particular, e.g. glycols, glycerols, paraffins with colorations below 100 Hazen and colour determination to the European pharmacopoeias, 50mm rectangular cuvettes can also be used. All colour measurements and colour number determinations with the LICO® 300 can be carried out with inexpensive glass or plastic disposable cuvettes with 10 mm, 11mm or 50 mm path length, thus eliminating the need for rinsing and cleaning. Sample volumes of only 3 to 5 ml are needed. If necessary, products with higher melting points, such as fatty acids or paraffins, can be heated with a small Dr. Lange thermostat before the measurement is carried out. With integrated test equipment monitoring and the use of certified test filters, LICO® 300 satisfies all the demands made on a quality assurance system to ISO 9000ff.

The simple instrument operation enables all conventional colour numbers to be determined. Measurements can also be carried out in line with the CIE L*a*b* system (DIN 6174), and all the usual photometric analyses in the wavelength range from 340 to 900 nm are possible. The existing data interfaces can be used to connect a printer or a PC.

C1.1 The spectral-QC PC-Software

LICO® 300 and 200 can be operated from a PC with the Dr. Lange ***spectral-QC*** PC software. The measurement values can thus be saved and documented with a sample name or a batch number.

All important data management functions such as displaying data and measured values or printing a file are also available.

Measured values can be converting to ASCII format and processed with a spreadsheet program.

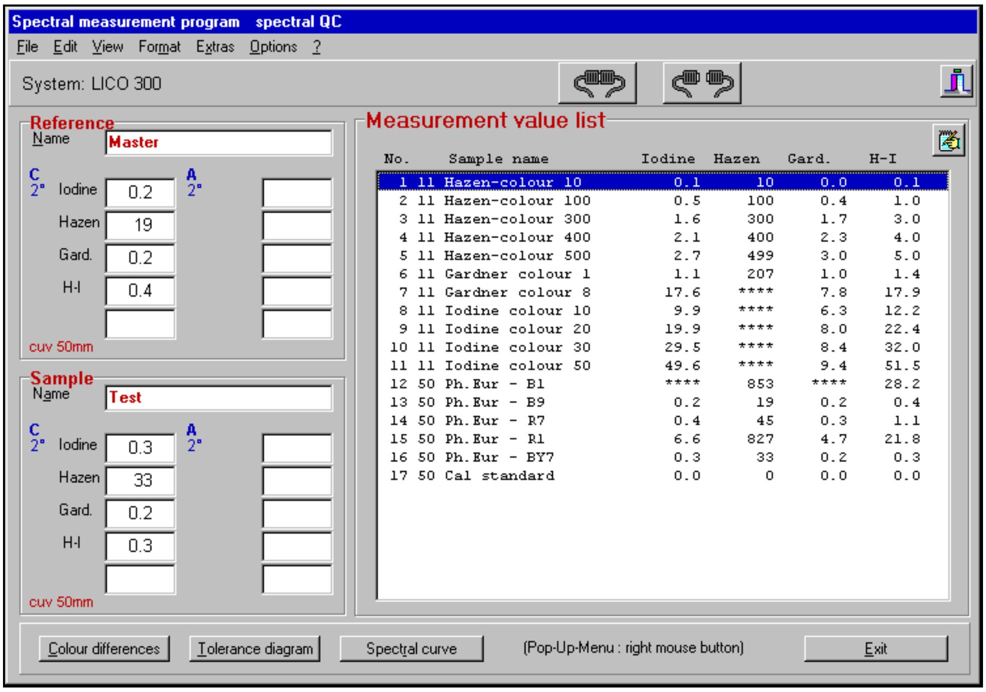


Fig. 15: spectral-QC for Windows®

For colour determination in conformity with the German or European pharmacopoeias a special window (Fig. 16) is opened under the menu item **'Extras/Ph.Eur. - determination'**. The window contains a field in which the user selects the desired colour scale B, BY, Y, GY, R or the default for evaluation. The sample is subsequently transferred to a cuvette, which is introduced into the LICO® and the colour measurement is started. The sample is assigned to the Ph.Eur. scale on the basis of the determined CIE-L*a*b* values.

The values of the colour reference solutions and the permissible tolerances are determined in the Dr. Lange reference laboratory and stored in the program. The program function "L*a*b*-diagramm" is used to display a section of the CIE-L*a*b* diagram, showing the colour scale, the tolerance limits and the colour location of the measured sample, depending on the selected colour reference scale.

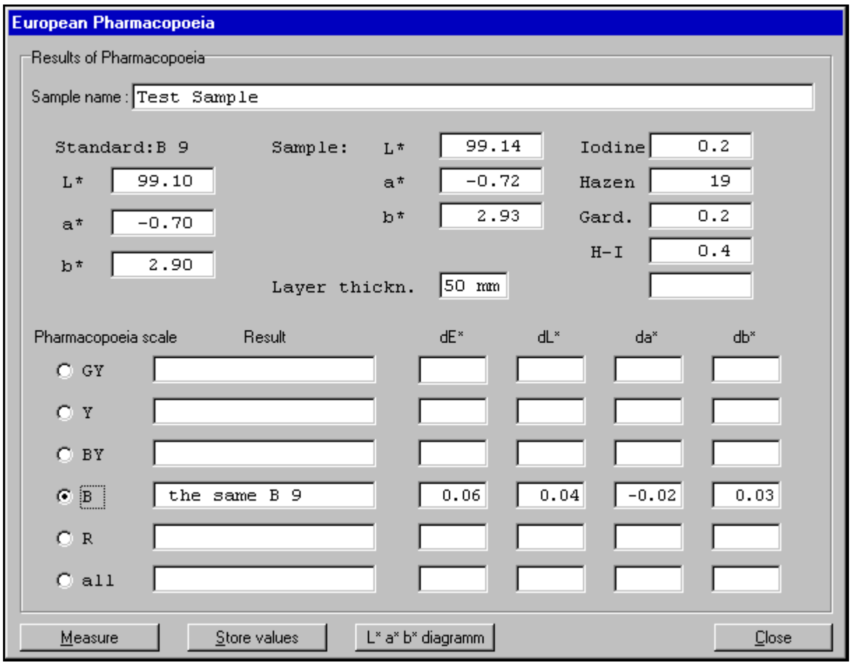


Fig. 16: Window for colour determination to Ph.Eur.

C1.2 LICO® 230

In 1991 the LICO® 200 from Dr. Lange created the basis for objective colour measurement. Today it is in worldwide use in more than 1000 laboratories and production companies.

Fig. 17: LICO® 200

The affordably priced LICO® 230 model is designed for production areas in which only one colour number has to be determined. The LICO® 230 can, however, be upgraded with more colour systems if necessary, e.g. if the production specifications change or the colorimeter is to be used at another site.

C2 The LICO® 100

The LICO® 100 is designed for fast routine measurements in the laboratory and in production facilities and is already in use in a wide variety of areas in the chemical, cosmetic and pharmaceutical Industries for quality and production control, e.g. to assess surfactants, oils, fats, resins and synthetic resins. It replaces traditional visual colour assessment by fast and objective measurements and can be operated either on battery power or with a power pack. An interface enables a Dr. Lange printer to be connected.

Fig. 18: LICO® 100

The LICO® 100 is supplied with the following colour systems: Iodine, Hazen, Gardner, Saybolt colour number and ASTM D 1500.

The measurement procedure starts automatically when the cuvette containing the sample (50mm rectangular or 11 mm round cuvette) is placed in the cuvette compartment. The precise, reproducible result is displayed in terms of the selected colour system. An automatic switch-off after a 20-minute idle period prevents the batteries from being run down unnecessarily. Simple operation, automatic calibration and the use of affordable disposable cuvettes make the LICO® 100 a cost-effective alternative to traditional visual measurement methods.

D Annex

D1 Test Media Inspection

Dr. Lange offers test filter sets for LICO® as certified test media for inspection. They comply with the requirements of ISO 9001ff regarding test certificate, reference values and permissible tolerances, serial number, calibration date, validity and signature.

Additional safety is offered by a maintenance agreement which does not only ensure good function of the instrument but comprises more advantages like e.g an extended guaranteed period of 5 years in total and free software-updates. Combined with these certified test media, Dr. Lange’s colorimeters are the best basis of a quality system in compliance with ISO 9000-9004 and GLP.

Fig. 19: Test filter set LZM 134 for LICO® 300/200/230

D2 Cuvettes and Accessories

Five cuvette types of three path lengths are at choice for colour determination. The cuvette is selected with regard to the colour intensity (water clear or tinted) and the type of sample (diluted, with solvent).

The cuvettes differ in material and path length.

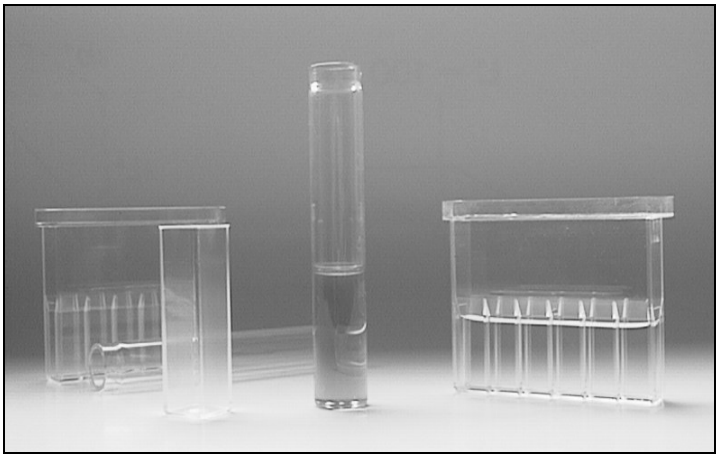


Fig. 20: Dr. Lange cuvettes

cuvette type	10mm glass	10mm PS[10]	11mm glass	50mm glass	50mm PMMA[11]
dimensions inner (mm) outer (mm)	 10 x 10 12 x 12	 10 x 10 12 x 12	 11,3 ∅ 13,2 ∅	 50 x 10 52 x 12	 50 x 5 52 x 12
filling volume approx.	2 ml	2 ml	2 ml	10 ml	5 ml
max. temperature	90° C	70° C	180° C	90° C	70° C
pieces/pack	1	1000	494	1	50
order no.	LYY 215	LYY 214	LYY 621	LYY 216	LZM 130

For the disposable 11mm round glass cuvette a dryer thermostate is available to warm up to 15 cuvettes to temperatures of 100°C or 148°C.

For colour measurements at foils, LICO® 300/200 can be supplied with a special foil holder.

Fig. 21: Foil holder

D3 References

[1] DIN 5033 Colour measurement.

[2] DIN 6174 Colorimetric evaluation of colour differences

[3] EN 1557 Colorimetric characterization of optically clear coloured liquids.

[4] DIN 6162 Determination of iodine colour number

[5] ISO 6271 Clear liquids;Estimation of colour by the platinum-cobalt-scale (Hazen, APHA colour number, also ASTM D 1045-58, ASTM D 268-49, ASTM D 1209-62, BS 2690:1956.).

[6] ISO 4630 Estimation of colour of clear liquids by the Gardner colour scale, also ASTM D 1544-80.

[7] Hess-Ives Bestimmung der Farbzahl nach Hess-Ives; DGK-Prüfmethode F 050.1.

[8] Ph. Eur European Pharmacopoeia, chapter ″Coloration of Liquids″

[9] ASTM D 156 Standard Test Method for Saybolt Color of Petroleum Products

[10] ASTM D 1500 Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale), also DIN/ISO 2049

[11] ASTM D 5386 Standard Test Method for Color of Liquids Using Tristimulus Colorimetry.

[12] ASTM D 6045 Standard Test Method for Color of Petroleum Products by the Automatic Tristimulus Method.

[13] ASTM D 6166 Standard Test Method for Color of Naval Stores and Related Products (Instrumental Determination of Gardner Color).

[14] AOCS Cc 13a FAC Standard Color.

[15] AOCS Cc 13e Fats and fatty oils, Determination of colour, also BS 684 1.14.

[16] Richter M. Einführung in die Farbmetrik, Verlag: Walter de Cruyter, Berlin, New York.

[17] Gohlke F.J Colorimetric Characterization, Tenside Detergents 23.Jg.86, ed. 4.

[18] Möller-Kemsa J. Objective Colour Assessment at Cosmetic Products, Euro Cosmetics 4/94.

[10] polystyrene

[11] polymethylmethacrylate

D4 Technical Data of Dr. Lange Instruments

Instrument	**LICO® 300**	**LICO® 230**	**LICO® 100**
measuring system	spectral	spectral	spectral
measuring geometry	0°/180°	0°/180°	0°/180°
standard illuminant	C	C	C
halogen lamp	12V/20W	12V/20W	6V/10W
reference beam path	•	•	•
cuvette compartment			
10mm-square cuvette	•	•	-
11mm-round cuvette	•	•	•
50mm-square cuvette	•	•	•
Automatic cuvette detection	•	-	•
GLP-conformable print-out	•	-	-
Integrated test media control	•	-	-
certified test media	•	•	•
evaluations/measuring ranges			
standard tristimulus values XYZ	•	•	-
chromaticity coordiates xyY	•	◊	-
CIE-Lab-values L*a*b*	•	◊	-
CIE-Lab-difference values	•	◊	-
Hunter-Lab-values	•	◊	-
Ph-Eur-computation[1)]	•	◊	-
transmittances Txyz	•	◊	-
Iodine colour number	0..120	◊	0..120
Hazen colour number	0..1000	◊	80...1000
Gardner colour number	0..18	◊	0..12
Lovibond® [2)] yellow/red	•	◊	-
Saybolt colour number	+30..-16	◊	+30..-16
Mineral oil colour number	0..8	◊	0..8
Klett colour number	0..1000	◊	-
Yellowness-Index	•	◊	-
Hess-Ives colour number	•	-	-
spectral transmission T_{380}-T_{720}	• / 10nm	◊	-
photometric functions			
scan 340nm..900nm	• / 1nm	◊	-
absorption 340nm..900nm	• / 1nm	◊	-
other functions / accessories			
plotter	✓, external	✓, external	✓, external
RS-232C-interface	•	•	•
PC-software	•	•	-

1) Determination of Tints of Liquids according to the European Pharmacopoeia
2) Lovibond® is a registered trademark of THE Tintometer® LTD, UK
◊ option

Subject to technical modifications

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