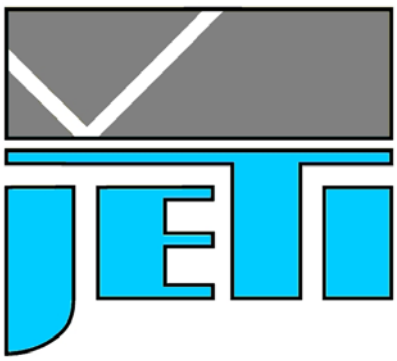
Basics of Spectral Measurement



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Introduction

Modern spectroscopic measurement equipment becomes smaller and more cost effective. Therefore, it is used in more and more new application fields besides the classical one in analytics. Spectroscopic methods are applied in research and production for color measurement, chemical analysis and quality control, pharmaceutical testing, medical check up, plant growth observation, testing of light emitting devices, food control, pollution measurement, etc. Currently, they are increasingly used in process control, e.g. in dye works, chemical plants, semiconductor industry and electro plating processes.

Table of Contents

1 Miniaturized Spectrometers

1.1 General Set-up

The classical spectrometer consists of an input slit, a rotating dispersive element (prism or grating), an output slit and a single detector. This arrangement allows the separation of multichromatic radiation into its spectral components. The main advantages are the high sensitivity and the low stray light. Several drawbacks, such as the non-parallel measurement, the moveable elements and the space consuming dimensions, were overcome by the development of array spectrometers. This kind of spectrometer uses a detector array instead of a single detector and therefore only needs fixed components. Meanwhile, they are widely used in PC coupled, stand-alone as well as hand held devices and begin to find their applications even in the online process measurement.

1.1.1 Gratings

Most of the time gratings are used as the dispersive element in array spectrometers. They have the advantages of higher dispersion and lower production costs than prisms. The basic grating equation is as follows:

$$\sin\Theta_m = \sin\Theta_i + m\frac{\lambda}{d} \qquad (1)$$

with θ_i and θ_m - angles of the incident as well as the diffracted wave directions to the normal of the grating surface, λ - wavelength, d - grating period and m - order of diffraction (integer value, m = 0, $\pm$1, $\pm$2, ...). This equation is valid for reflexion gratings, whose grooves are perpendicular to the plane of incidence. Gratings in spectrometers are mostly used in reflectance mode.

The equation shows, that for m $\neq$ 0 the radiation of different wavelengths is separated angularly. This effect is called dispersion. Furthermore, each wavelength is diffracted into different discrete angles according to the order m, causing an ambiguity. Spectrometers usually use the dispersed light of one order. Influences of other orders and the non-dispersive zeroth order have to be suppressed. Fig. 1 shows the angular separation for monochromatic and polychromatic radiation, caused by a grating.

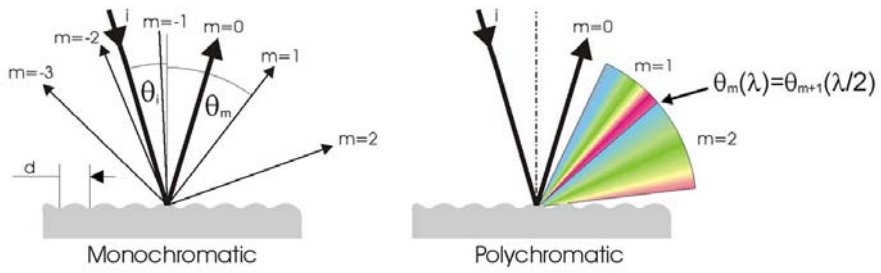


Fig. 1 Angular separation of mono and polychromatic radiation

It demonstrates the overlap between the different orders - the diffraction angle for m = 1 in the red region coincidences with the corresponding angle of half of the wavelength for m = 2. The free spectral range (range without overlap) becomes smaller for higher diffraction orders.
As mentioned above, the order of diffraction can have negative or positive values. The common convention, also used here, calls the order positive, if the angle of diffraction exceeds the angle of incidence and lies on the opposite side of the grating normal.
The grating equation determines the angles of diffraction, but has nothing to do with the intensity distribution into the different orders. The fraction of light intensity diffracted in one order, related to the entire incident intensity is called diffraction efficiency of this order. Symmetric profiles as the sinusoidal shape of the gratings in fig. 1 are not very effective. The efficiency can be tuned by varying the shape and depths of the grooves. An increased efficiency is obtained by a saw tooth profile. The angle of the swots has to satisfy the condition of the regular reflexion law to reflect the incident beam into the angle of the chosen diffraction order. This is called blazing and the condition can be met exactly for one wavelength only, the blaze wavelength. It is practical to lay this wavelength in the region, where the other components of the system have low effectivity, e.g. the light source or the detector, to achieve a homogenisation of the system's performance.
The change of diffraction angle corresponding to a small change in wavelength is called angular dispersion of a grating. The following equation is obtained by differentiating the grating equation to the wavelength with fixed angle of incidence:

$$\frac{d\Theta_m}{d\lambda} = \frac{m}{d \cdot \cos\Theta_m} \qquad (2)$$

The linear dispersion dl/dλ is the product of the exit focal length f of the spectrometer and its angular dispersion:

$$\frac{dl}{d\lambda} = f \cdot \frac{d\Theta_m}{d\lambda} = \frac{f \cdot m}{d \cdot \cos\Theta_m} \qquad (3)$$

It defines the extend of the spectrum on the detector array.

1.1.2 Spectrometer Set-up

Array spectrometers consist of an input slit, a grating, possibly other optical imaging elements, a line detector and a stable housing. Several basic optical arrangements are used for spectrometers. The basic demand for the design is to use collimated light for the dispersion - this improves the measurement accuracy. One can distinguish between plane grating set-ups and concave grating spectrometers. The latter type combines diffraction and imaging in one element. If plane gratings are applied, it is necessary to use additional optical elements for beam shaping, preferably spherical or aspherical mirrors for ray collimation and focusing.

The following figures show examples for both types of set-up (so-called mounts).

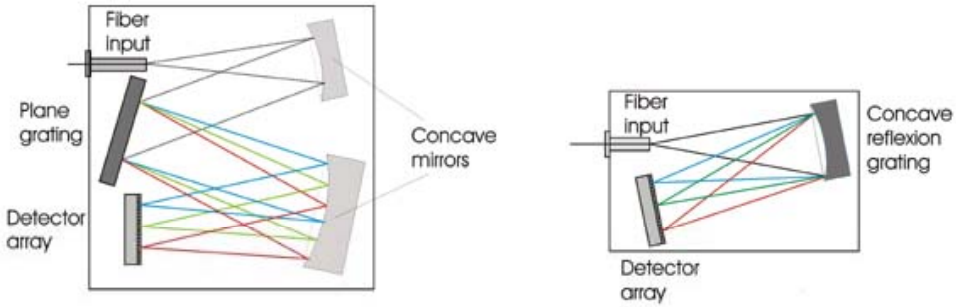


Fig. 2 Schemes of Czerny-Turner and flat field concave grating spectrograph

The advantages besides the lack of moving parts are the quasi-parallel measurement of the whole spectrum, which reduces the measuring time. Further advantages are the robustness and the small dimensions. The flat field arrangement is further advantageous because of fewer optical elements, which have to be adjusted. This type of grating offers a plane focal line, which can be detected by the plane detector array without remarkable focusing errors.

Nevertheless, plane grating spectrometers as the Czerny-Turner show improved optical properties because of better compensation possibilities of imaging errors. Usually, the most efficient diffraction order of the grating is detected by the array; the detection of other orders is avoided by design or suppressed by several means (filters, ray traps).

One has to say, that array spectrometers show some disadvantages, too: The integral illumination over the full wavelength range increases the stray light, compared with monochromatic set-ups. Furthermore, the sensitivity is lower than of a monochromator, which can even be fitted out with a photo multiplier. The precision and resolution is normally less than that of laboratory instruments with a turnable dispersive element.

The first array spectrometers included original gratings, manufactured by holography (interference of a splitted laser beam) or mechanical ruling. Holographic gratings show less stray light because of their better surface quality than those of mechanically proceeded ones. Furthermore, it is possible to produce holographic gratings with reduced imaging errors by a special design of the exposure arrangement.

Such master gratings are replicated into epoxy layers (with an aluminium reflexion layer and a protection coating) to reduce the costs of the spectrometer. A further price reduction is obtained with a replication of the master gratings by injection moulding into a plastics material, e.g. PMMA. This technique is useable for less demanding applications because of a deterioration of the optical properties.

The light inside the spectrometer commonly propagates in free space (air or glass). The Zeiss spectrometer is an example for this design.

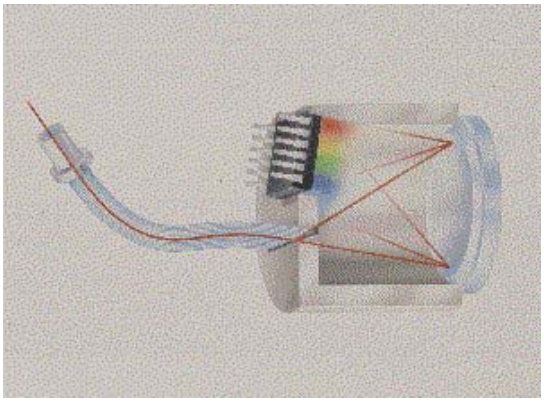


Fig. 3 Free space spectrometer MMS UV (Carl Zeiss Jena)

Another kind of spectrometer is based on the propagation in a slab wave guide (the LIGA spectrometer. This solution offers the possibility of an extreme miniaturization. This spectrometer, offered by STEAG microParts GmbH (Germany), is shown in the following figure.

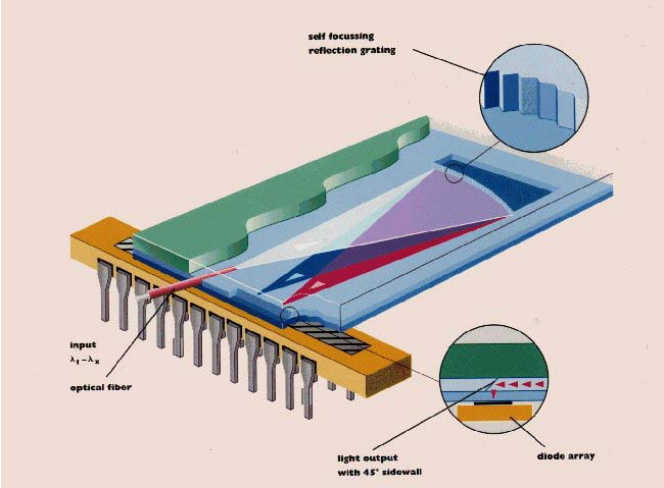


Fig. 4 Waveguide VIS spectrometer (STEAG microParts Dortmund)

Modern array spectrometers are often fitted out with a fiber optic input for a more convenient adaption to the measuring problem. There are used single multimode fibers with or without an additional slit or fiber bundles designed as cross section transformer from cylindrical to rectangular (slit) shape. In this case the input slit width w is determined by the fiber core diameter.
The detectors used in UV/VIS spectrometers are silicon-based CCD or photodiode arrays. CCD arrays show a higher sensitivity, but diode arrays offer a much better dynamics. The proper selection of the detector array for a special application can improve the performance of the whole system or can just make it possible. Further information about the function and the application oriented selection of detector arrays can be obtained from chapter 2 of these basics (Line Arrays for Miniaturized Spectrometers).

1.2 Spectrometer Parameters

1.2.1 Wavelength Range

Array spectrometers are available for wavelengths from the UV (200 nm) and VIS to IR (...3 µm). Wavelength ranges of commercial array spectrometers are indicated in the following figure:

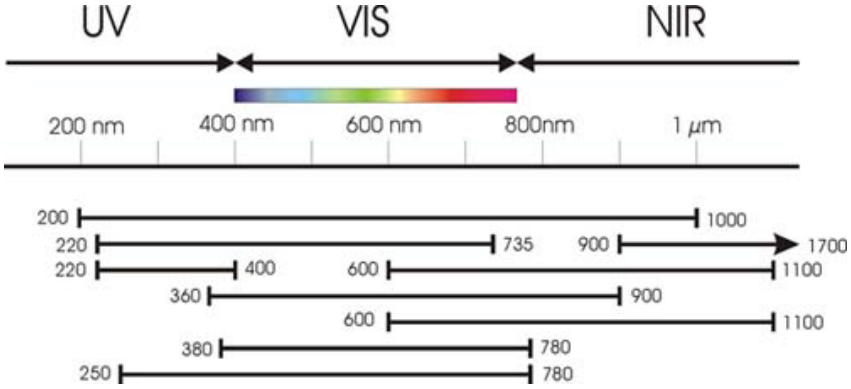


Fig. 5 Scheme of partial electromagnetic spectrum and of wavelength ranges of commercial spectrometers

The size of the spectrometer is determined by the wavelength range in connection with the desired optical resolution (see below), demanding in a certain focal length. JETI´s series of specbos instruments currently cover the range of 380 ... 760 nm, specbos 1000 UV covers 240 ... 480 nm and the JETI speclight series cover 350 ... 850 nm.

1.2.2 Resolution

Several definitions are used for the resolution of a spectrometer. One has to distinguish clearly between the optical or spectral and the digital or pixel resolution.

The **optical resolution** $\Delta\lambda$ is defined by the wavelength difference of two peaks close together in one spectrum and of same intensity, which can be separated. The dip between the peaks has to reach a minimum of at least 19 %, related to the maximum intensity. This definition is called the Rayleigh criterion.

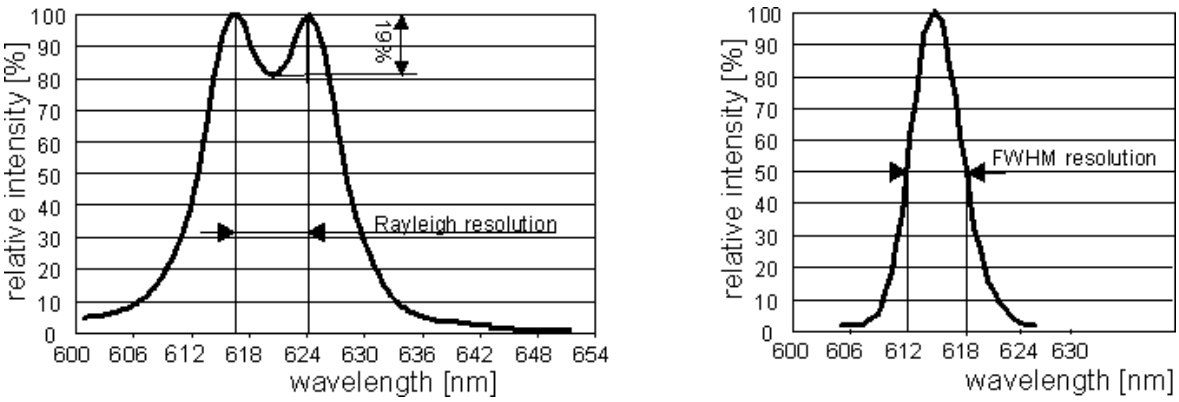


Fig. 6 Definition of the optical resolution (Rayleigh and FWHM)

Another more practical definition is related to the measured width of a narrow spectral line. Its measured bandwidth $\Delta\lambda_{FWHM}$ gives information about the broadening of the line. This bandwith amounts to about 4/5 of the resolution according to the Rayleigh criterion.
The optical resolution is determined by the width of the input slit, the focal length of the optical system and the dispersion of the grating. $\Delta\lambda_{FWHM}$ is inversely proportional to the linear dispersion dl/dλ and directly proportional to the output slit width w´:

$$\Delta\lambda = w' \cdot \frac{d\lambda}{dl} \qquad (4)$$

This equation can easily be used for the estimation of a spectrometer resolution, especially with 1:1 imaging, where the width of the input slit equals to the width of the output slit (w = w´). The smaller the slit width, the higher is the resolution. However, reduced slit width reduces the optical energy, entering the spectrometer, too. This can cause sensitivity problems for a spectrometric system. Common resolution values of miniaturized VIS spectrometers ay in the region of 5 .. 12 nm, values even below 1 nm are possible. The core diameter of the input fiber influences the optical resolution, if it acts as the input slit.
A separate parameter is the **pixel or digital resolution**. This is the spectral bandwidth, which is detected by one pixel of the array and is determined by the width of the pixel and the dispersion of the spectrum. Common values are 2 ... 10 nm/pixel. JETI spectrometers are available with 2 to 10 nm/pixel. The digital resolution is related to the spectral resolution via the imaging properties of the spectrometer. The ratio of digital to spectral resolution should be ≥ 3 to detect safely a peak in the spectrum.

1.2.3 Stray Light

Stray light is radiation of false wavelengths, which strikes a pixel of the detector array. It is caused by imperfections of the grating, dust, reflexion of the spectrometer housing or errors of the other optical elements. This parameter influences the precision of a spectroscopic measuring system in a decisive way. It gets measured by a broadband illumination of the input slit through a color filter with long pass characteristics. A filter commonly used therefore is the Schott glass GG 495. The stray light S is the ratio of the transmission in the blocked wavelength region below the filter edge (τ(420 nm)) to the transmission in the non-blocked region (τ(600 nm)).

$$S[\%] = 100\% \cdot \frac{\tau(420nm)}{\tau(600nm)} \qquad (5)$$

It shows the influence of the light of longer wavelengths, passing the filter, on the unwanted intensity in the blocked region. A measured spectrum is shown in the following figure.

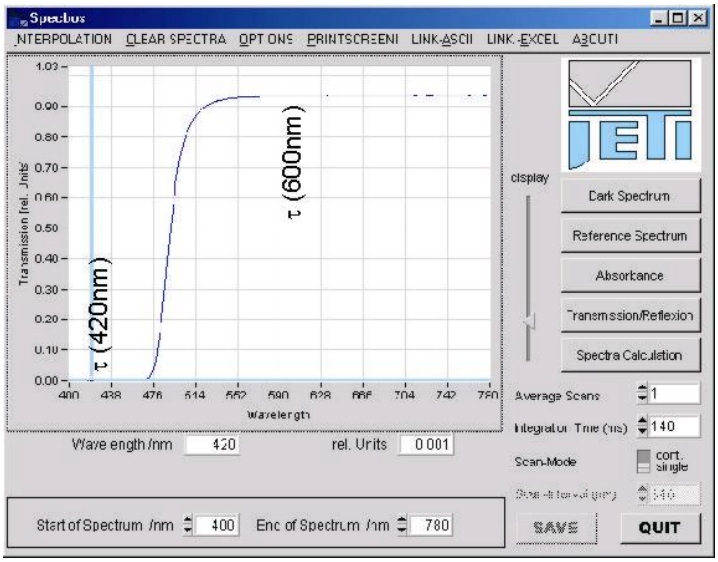


Fig. 7 Measurement of stray light

In case of a low stray light level (as in fig. 7) an additional neutral density filter is used for the measurement in the non-blocked region, which will be removed for the measurement in the blocked region.

$$SL[\%] = 100\% \cdot \frac{\tau(420nm) \cdot \tau(NDfilter)}{\tau(600nm)} \qquad (6)$$

A standard measurement method is described in the ASTM standard test method E 387 (available from www.astm.org). Detailed information about modifications of the measurement procedure and their influence on the result can be obtained from the Agilent technical note "Measuring the stray light performance of UV-visible spectrophotometers" (available at: www.chem.agilent.com/scripts/Literature Search. asp).
Another often used stray light measuring method uses a monochromatic light source (e.g. a HeNe laser). The intensities at the laser wavelength and at another wavelength, several 10 nm away from the laser wavelength are measured. The ratio of the latter to the former is a measure for the stray light of the system. This measuring method delivers much better values, but is more distant to the main practical applications, where a broadband illumination is used. Therefore, the method, described first, is recommended.
The stray light causes a non-linearity of the signal at lower power levels and thus limits the measuring range of the system. For example: the signal in the blue region of a VIS spectrometer depends on the incident intensity in the other regions of the spectrum. This effect cannot be compensated precisely by mathematical calculations in the software.
Every specification of stray light has to be given in connection with the used measuring conditions. One has to keep in mind, that the higher the bandwidth of the light entering the spectrometer, the higher the measured stray light ratio. The value, measured with a long pass filter with an edge in the red region of the spectrum is not comparable with a value, measured with a yellow edge filter (see the following figure).

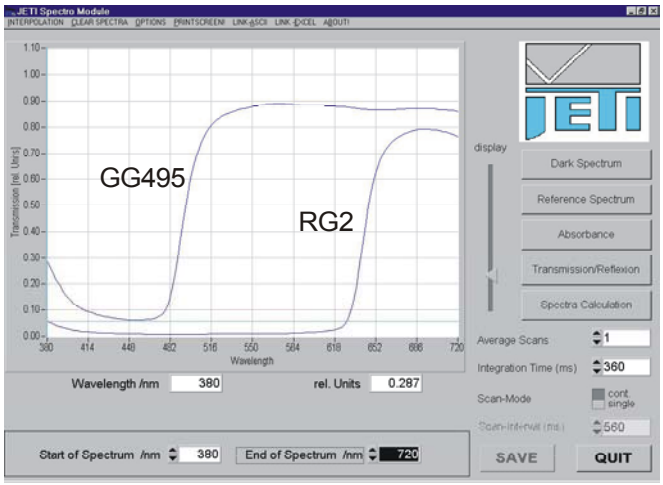


Fig. 8 Stray light measurements with GG 495 and RG 2

The stray light of array spectrometers is mainly higher than of monochromators due to the lack of an output slit.

1.2.4 ADC Resolution

The analog intensity distribution of the optical spectrum on the detector array has to be converted pixelwise to a digital signal by an analog digital converter (ADC). Common electronic resolutions are 12 ... 16 bit (4095 ... 65 535 counts full scale). These numbers are finally reduced by the dark spectrum of the line array and the driving of the converter. The ADC resolution should be in a suitable ratio to the stray light of the spectrometer and to the dynamics of the detector array. The dynamics D of the entire system is determined by the ADC resolution R_{ADC}, divided by the noise signal Φ.

$$D = \frac{R_{ADC}}{\Phi} \qquad (7)$$

A 12 bit spectrometer with a noise signal of 4 counts offers a dynamics of about 1000.

1.2.5 Integration Time

The light intensity coupled into a spectrometer and illuminating a pixel, results in a proportional signal from the AD converter. The exposure time of the light to the pixel is called integration time and is a main parameter to adjust the ADC signal. A level between 2/3 and full scale is suited for best measuring results, using the full dynamics of the system. Off scale peaks or regions in the spectrum have to be avoided. Common values for the integration time of array spectrometers are 20 ... 5000 ms. Several instruments, as the JETI spectroradiometer, specbos 1200, specbos 1201, speclight 1000 and speclight 2000, are equipped with an automatic integration time adaption.

1.2.6 Spectral sensitivity

The sensitivity of a spectroscopic system E(λ) is another important issue in many applications, especially in fluorescence detection, and is a main criterion for the choice of a spectrometer. It is measured in counts/ Ws and means the ADC signal r [counts] divided by the optical energy P (λ) · t_{int} [Ws], entering the spectrometer optical input.

$$E(\lambda) = \frac{r}{P(\lambda) \cdot t_{\text{int}}} \qquad (8)$$

The spectral sensitivity has to be specified for a given wavelength mainly because of the spectral dependencies of the grating efficiency and the detector sensitivity. The measurement can be done with bandpass filtered white light illumination or a monochromator, from which the radiant flux P (λ) is known.
Furthermore, sensitivity data have to be related to the ADC resolution of the read out electronics. The main uncertainity in sensitivity measurements is caused by the measuring error of P (λ), coupled into the spectrometer.
The spectral sensitivity can be adapted in certain limits to the application by a proper selection of the spectrometer's detector array (see chapter 2 "Line Arrays for Miniaturized Spectrometers").

1.2.7 Wavelength and Intensity Calibration

The AD converter delivers the spectral signal in counts for each pixel. The pixels are numbered and these numbers have to be transformed into the corresponding wavelength. This can be done by a multiorder polynom as follows:

$$\lambda(n) = k_0 + k_1 \cdot n + k_2 \cdot n^2 + k_3 \cdot n^3 + \ldots + k_i \cdot n^i \qquad (9)$$

where n is the pixel number, k_0 [nm] the wavelength of the first pixel, k_1 [nm/pixel] the pixel resolution and k_2, k_3, .., k_i are the higher order coefficients.
This approximation with a polynom gives a wavelength precision, which has to be taken into consideration in the application. The choice for the order of the polynom depends on the non-linear behaviour of the spectrometer. The linear approximation is sufficient for a LIGA Spectrometer, whereas a higher order polynom is necessary for the Zeiss MMS.
The calibration can be done by relating the peaks of a suited spectral lamp (e.g. Hg in the VIS range) to the corresponding pixel and subsequent calculation of the k-parameters by regression (e.g. in Excel). JETI offers a special fit program for this purpose. This program can be used to measure the spectra, indicate the peaks, calculate the k-parameters and check the result. A spline fit is used to get a subpixel precision.
A easy way to check the calibration of a spectrometer for somebody who has no special spectral lamp is to use a common fluorescent lamp (F11, possibly on top of the lab), which has a spectrum as shown in the following diagram. The intense peaks of 546 and 614 nm can be used for a roughly test of the calibration.

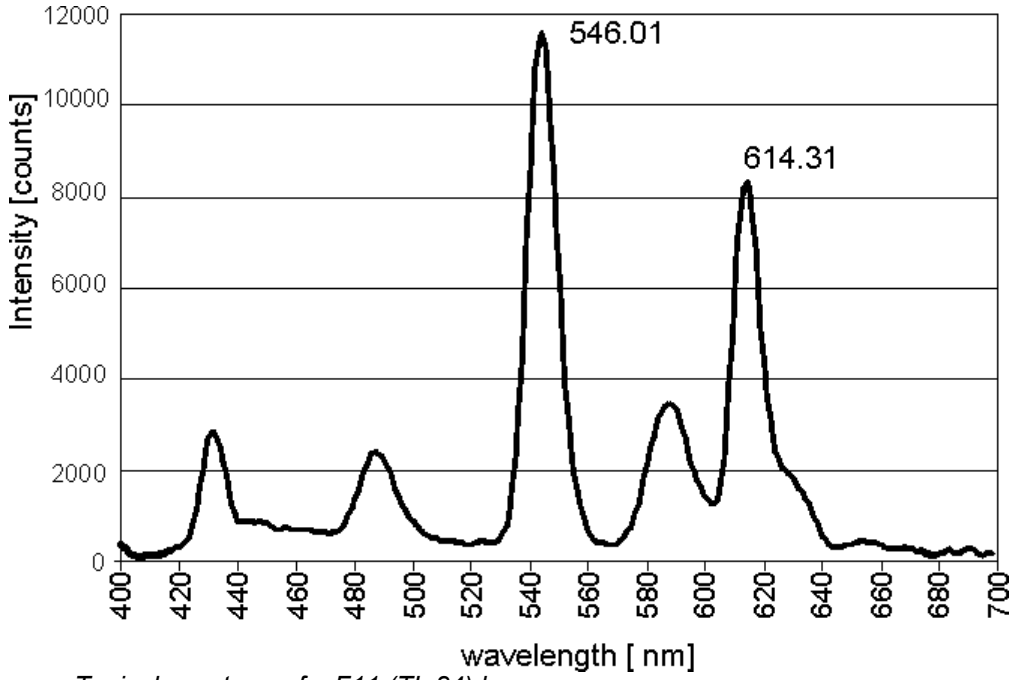


Fig. 9 Typical spectrum of a F11 (TL 84) lamp

Something else, sometimes mixed with the wavelength calibration, is the calibration of the intensity axis. A non-calibrated spectrometer as the JETI specbos 1000 has an intensity axis (y- axis) in counts or percent. Therefore, only relative measurements of light sources, e.g. the spectral distribution of LED, are possible. One has to keep in mind, that the obtained spectrum is weighted with the instrument function (grating efficiency, transmittance, detector sensitivity).

2 Line Arrays for Miniaturized Spectrometers

The line array of a spectrometer is, besides the grating, the main parameter determining part. A suited choice of the array is vital for the proper adaption of the system to a certain application. The kinds of line arrays and their operation principles as well as issues for a correct selection are described in this chapter.

2.1 General Description

Line arrays are detectors with several individual readable sensitive areas, so-called pixels (picture elements), arranged in one straight line. They can be seen as “black boxes” transforming a spatially light distribution, in case of spectrometers the spectrum focus line, into a signal voltage or current distributed in time. This sequential output signal, the video signal, is further proceeded, mainly with an analog digital conversion as the first step.

The main parameters of line detectors are the following:

- Pixel number – the number of pixels arranged in the line
- Pixel dimensions – the pixel width and height [µm]
- Pixel pitch – the distance between the centers of two pixels [µm]
- Sensitivity – the wavelength dependent ratio of electrical signal output to the optical signal input [e.g. V/lx·s]
- Wavelength range – the range of wavelengths where the detector can “see” radiation [nm]
- Dark signal – the output signal without illumination of the detector [e.g. mV]
- Saturation exposure – the illumination level, at which the output signal stays constant with increasing illuminance [e.g. mlx·s]
- Linearity range – the illuminance range where the electrical signal output is proportional to the impinging energy [e.g. mlx·s]
- Dynamic range – the range in which the detector is capable of accurately measuring the input signal [10^x]
- Pixel non-uniformity – the output signal difference of the pixels under same illumination conditions [%]

Furthermore, the following issues are of interest for an application:

- the scheme of the operation pulses (every line detector needs several clocks for the read out operation)
- the thermal behavior of the array
- the image lag – a property of line detectors to “remember” the illumination of previous read out’s

2.2 Types of Line Arrays

Currently, there exist three different types of line arrays, which are used in spectrographs: CCD, photodiode and CMOS arrays. They differ in their distinct production technologies and their parameters.

2.2.1 CCD Arrays

Principle of Operation

CCDs are array detectors with metal-oxyde capacitors (photogates). During the illumination by the spectrum focal line a charge (electron – hole pairs) is produced under the gate. A potential well is created by applying a voltage to the gate electrode. The charge is confined in the well associated with each pixel by the surrounding zones of higher potential (see detail in fig. 10). The read out of the array is proceeded by a charge transfer by means of varying gate potentials according to special clock schemes. The charges of the pixels are transfered simultaneously to the shift register(s), followed by a sequential transfer to the output section, where the charge is converted into a proportional voltage. The node doing this is first set to a reference level (clamp level) and afterwards to the signal level. The difference is used as the final signal. This technique is called Correlated Double Sampling (CDS) and allows a significant reduction of the system noise.

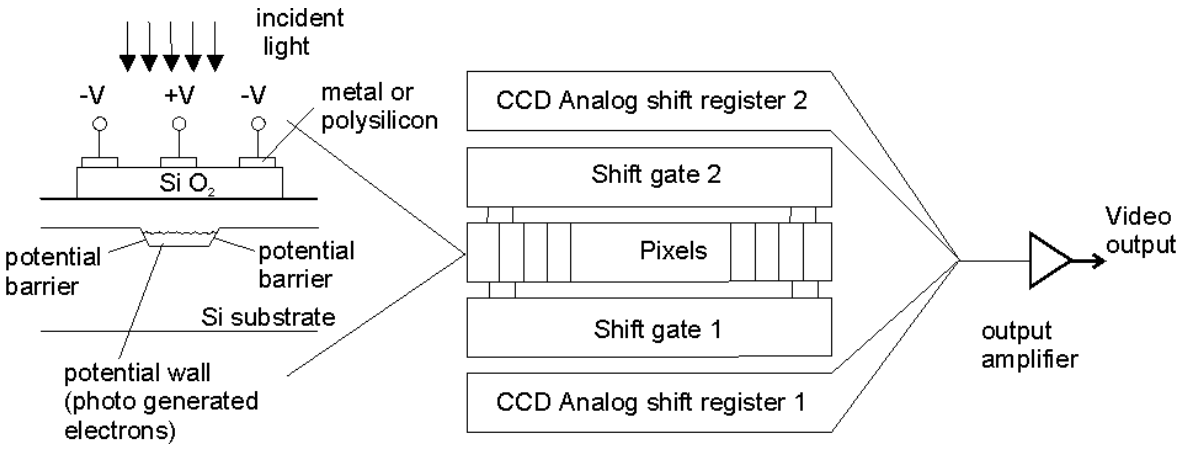


Fig. 10 Operation principle of a CCD array detector

Examples (see table at the end of this chapter)

There exists a wide variety of CCD arrays from several producers. The Sony ILX series is often applied in spectroscopy. Other types are the TCD 1201D of Toshiba and the S 703x series of Hamamatsu. The latter has not only one pixel line but also 122. It can be used in the so-called line-binning mode. The signals of each pixel row in the direction perpendicular to the spectrum are additionally combined to create a greater pixel height.

2.2.2 Photodiode Arrays (PDA)

Principle of Operation

Photodiode arrays consist of several photodiodes arranged in a line. The light energy impinging on a diode generates a photocurrent, which is integrated by an integration circuitry associated with this pixel. During a sampling period the sampling capacitor connects to the output of the integrator through an analog switch.

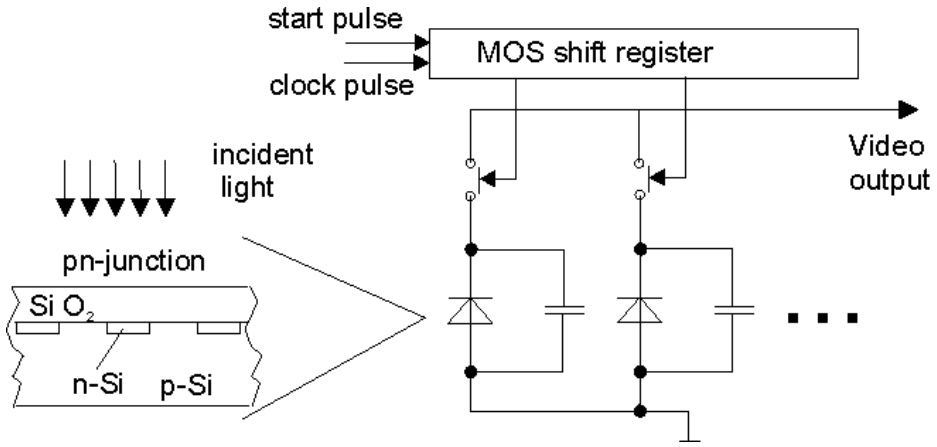


Fig. 11 Operation principle of photodiode arrays

There exist two different types of photodiode arrays which differ by kind of their output signal.

Current output arrays supply the recharge current of the depletion layer capacity as measuring signal. Therefore, an additional integrator is necessary. The relation between the peak value of this current and the integral is poor, so read out electronics based on the reading of the peak value are of lower quality. Especially with low saturation charge, it is difficult to measure the output correctly. A value of 1 pC equals about 10^7 electrons, with an electronic resolution of 16 bit one LSB is represented by only 1 000 electrons.

Voltage output arrays have the integrator on board and deliver a photon flux proportional voltage for the measurement. This causes fewer problems with the read out electronics.

Examples

Examples are the S 39xx and S 838x series of Hamamatsu as well as the MLX 90255 of Melexis and LF2C of IC Haus.

2.2.3. CMOS Arrays

Principle of Operation

CMOS arrays also use MOS structures as pixels like the CCD arrays. The basic difference is, that the charge-to-voltage conversion takes place directly in the pixel cell. This conversion consists again of two steps – the photon – electron and the charge (electron) – voltage conversion. This difference in read out technique has significant implications for the sensor architecture, capabilities and limitations. The following figure shows the scheme of a CMOS line array.

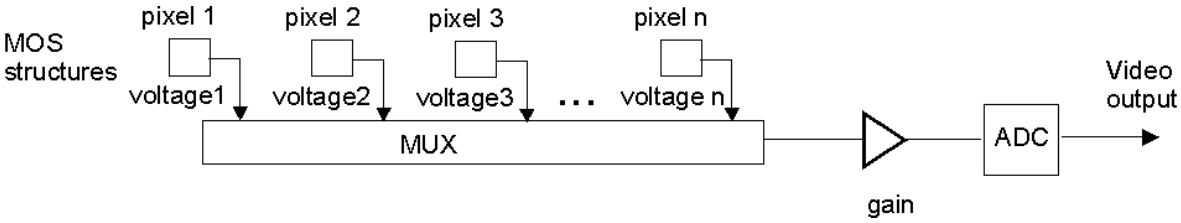


Fig. 12 Operation principle of CMOS arrays

CMOS arrays show better sensitivity than CCD's because it is easier to produce low power high gain amplifiers in CMOS technology.

Examples

The S 546x series of Hamamatsu and the L series of Reticon are examples for CMOS detectors.

2.3 Criteria of Selection for a Specific Application

As stated above, there are many parameters to consider for a proper selection of a line array for a specific application. Furthermore, it is necessary to weight the significance of the parameters because there is often no ideal choice possible.

Wavelength Range and Sensitivity

The detectable wavelength range of silicon-based arrays extends from 200 to 1100 nm, above this limit the photon energy is lower than the band gap energy. For longer wavelengths, InGaAs semiconductor material is used (up to 1.7 µm). Such arrays are relatively expensive. Furthermore, Si line arrays with anti Stokes Phosphor coatings are available. They are suited for the wavelength range up to approximately 1600 nm (depending on the material).

If we consider only silicon arrays there are also differences between the different types of arrays caused by the set-up and technical treatment. Mainly the extend of sensitivity in the range below 380 nm and above 800 nm differs significantly. The window material often is a limiting factor in the UV range. Therefore and due to the avoidance of additional Fresnel reflexes in the system detector, arrays in spectrometers are often used windowless.

The following figure shows the relative sensitivity of several line arrays.

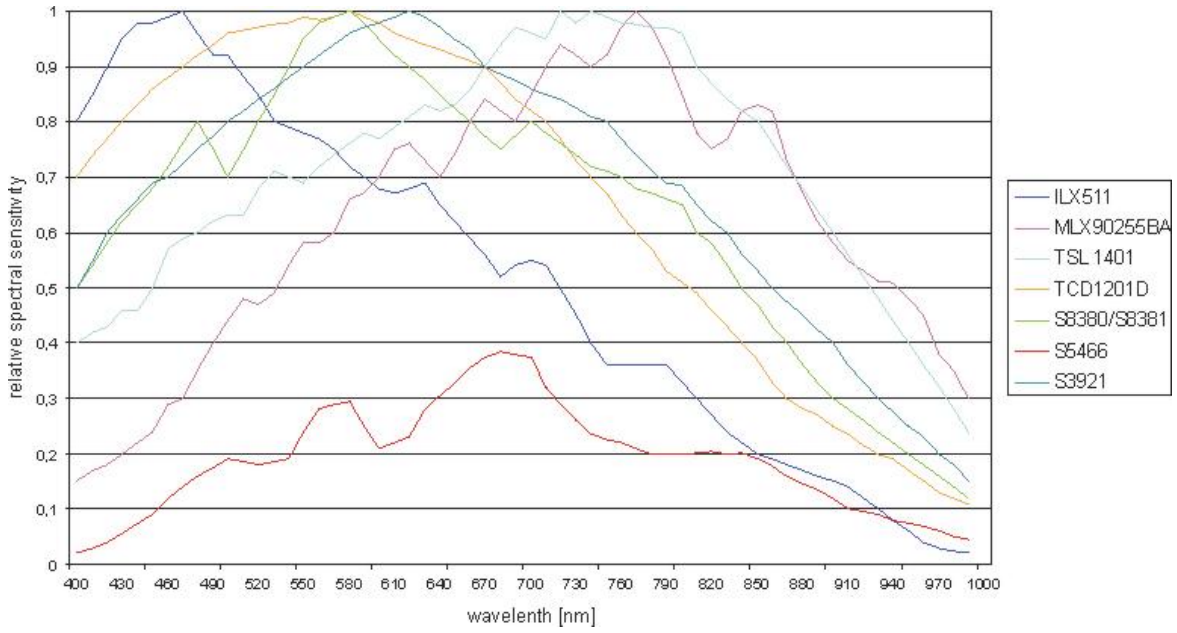


Fig. 13 Relative sensitivities of selected Si line arrays

The periodic modulation in many sensitivity curves is caused by white light interference on thin layers in the sensitive area and can be avoided by antireflexion coatings.
Typical absolute sensitivity values of different line arrays are shown in the following table:

Line Array	**Typical Sensitivity**
Hamamatsu S546x series	5.3 V/(lx·s)
Sony ILX 5x1 series	200 V/(lx·s)
TAOS TSL 140x series	25 V/(µJ/cm^2 = 171 V/(lx·s) @ 550nm
Toshiba TCD 1201D	80 V/(lx·s)
Melexis MLX 90255	1.3 V @ 10 µW/cm^2 @ 0.7 ms
Reticon L series	2.9·10^{-4} C/(J·cm^2)

Pixel Dimensions (pitch and height)
The pixel dimensions are an essential criterion for the selection of an array. The pixel width and pitch influence the digital resolution of a spectrometer and stand in relation to its optical resolution (see chapter 1.2.2.). Furthermore, it is necessary to adapt the pixel height to the height of the spectrum image. If the pixel height is too low, a part of the signal is lost and the efficiency of the system is low. On the other side a pixel height much larger than the spectrum height ends in an unwanted increased stray light influence. Some 2 – dimensional arrays allow a line binning for the virtual creation of a bigger pixel height.

The pixel line has to be precisely adjusted to the spectrometer focal line to avoid a strong thermal drift of the intensity output. Therefore, JETI offers a special light source JLQ 1, which simultaneously emits three wavelength ranges in the blue, green and red into one fiber. The three outputs are controllable, this can be used with a precise mechanical positioning of the array in 3 directions (parallel and perpendicular to the pixel line as well as the angle between spectrum and pixel line) for a precise adjustment.

Dark Output

The dark output is a small electrical output of the line array without incident light. It is caused by thermal generation of carriers in the light sensitive elements, mainly due to Si – SiO_2 interface states. It has a strong correlation with the operation temperature. The dark output doubles for every temperature increase of 6 ... 10 K. Therefore, line arrays are cooled in low light level applications, e.g. in astronomic measurements.

Furthermore, the dark output depends on the integration time. Therefore, it is necessary in spectroscopic measurements to proceed a dark measurement at the same integration time which is used for the spectrum measurement. This can be done by a mechanical shutter (e.g. JETI spectroradiometer specbos 1201) or with a switched off light source (e.g. JETI colorimeter specbos 4000).

The dark output level of the spectrometer electronics has a relative niveau. It can be moved by the choice of gain and offset settings.

Saturation and Linearity Range

Saturation exposure is that level of photon intensity where the photon signal of the detector is no more dependent on the incident light flux. The value depends on the doping of the detector material. A rule of thumb is that a good linearity is achieved with photodiode and CCD arrays modulated between 0 and approximately 75 % of the saturation charge (exposure). Above this value the non-linearity raises significantly. The following figure shows the linearity behavior of a current and a voltage output photodiode array.

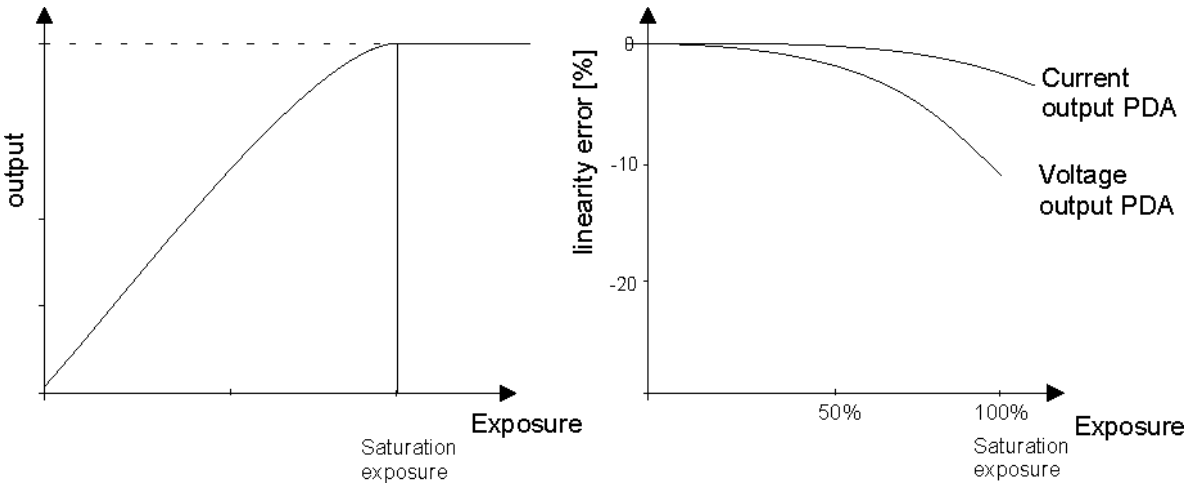


Fig. 14 Linearity behaviour of two line arrays (Hamamatsu)

The saturation exposure is given in the array data sheets, [mlx·s] and [nJ/cm^2] are used as units, depending if it is seen from a photometric ar a radiometric point of view.
The following table shows some values:

Line Array	**Typical Saturation Exposure**
Hamamatsu S 390x series	180 mlx·s = 26.3 nJ/cm^2 @ 550 nm
Hamamatsu S 392x series	220 mlx·s = 32.1 nJ/cm^2 @ 550 nm
Hamamatsu S 837x series	145/570 mlx·s =21.2/ 83.2 nJ/cm^2 @ 550 nm
Sony ILX 5x1 series	40 mlx·s = 5.8 nJ/cm^2 @ 550 nm
TAOS TSL 140x series	92 … 140 nJ/cm^2
TAOS TSL 1301	7 nJ/cm^2
Reticon L series	35 nJ/cm^2
PVs ELIS-1024	800 .. 6400 Ke$^-$ full well (dep. from selected pixel width)

Noise and Dynamics
There are two main categories of sources, which generate noise in a line array.

1. Fixed pattern noise
   It consists of the dark noise and read out noise (e.g. due to internal switching). The fixed pattern noise is constant when the read out conditions are fixed and the integration time is not changed. So it is possible to eliminate it by subtraction from the measured signal.
2. Random noise
   It is traceable to erroneous fluctuations of voltage, current or electrical charge, which are caused in the signal output process. If the fixed pattern noise is subtracted, the random noise determines the lower limit of light detection or the lower limit of the system dynamic range.

The dynamics is that range in which the detector is capable of an accurately measurement of the signal and is defined as the maximum detectable signal divided by the minimum signal level. The maximum detectable signal is limited by the detector saturation, the minimum signal by the noise of the system.
The dynamics depends on the integration time due to the thermal generation of noise.
Every kind of photon detectors only reaches a typical dynamics. Standard CCD arrays, like the Sony ILX 511, show a dynamics of 250 ... 300, related to full scale driving. If the spectrum has also regions with lower signal levels, the dynamics becomes even lower in these regions.
The dynamics of photodiode arrays is much higher. It depends on the operation regime and is determined by the analog multiplexer on chip and the integrators. Dynamics values of > $3 \cdot 10^4$ can be reached with the Hamamatsu S39XX photodiode array series at room temperature, if it is used with a low noise

integrator amplifier and a subsequent high performance 16 bit ADC. Photodiode arrays with integrator on board show a lower dynamics in main cases. An essential condition for a high dynamics is a high saturation charge of the array.
In case of minimum speed demanding applications it is possible to increase the dynamics by averaging.

Temperature Drift of Sensitivity and Dynamics
There are two effects, which cause a significant temperature dependence of the detector sensitivity: The absorption coefficient increases slightly with temperature. This effect increases the IR efficiency, but conversely decreases the UV efficiency. The second more significant effect is the exponential increase of the thermally excited electron-hole pairs with temperature. This leakage current doubles every 6 ... 10 K increase in temperature, connected with a raising noise.

Pixel Non-uniformity
The individual pixels of an array have different sensitivities caused by crystal flaws in the substrate and slight local variations in the wafer process. This uniformity is measured during a uniform illuminance of the sensitive area (50 % of saturation exposure) and calculation of the maximum deviation from the average value. Often the pixel non-uniformity is not of interest, especially if spectrometric systems are referenced. Thus the specific pixel differences are included in this reference.

Integration Time
The integration time is the main parameter for the user to adapt the modulation of a spectrometric system to the signal level of the measurement. In many applications it is necessary to have a linear relation between the integration time and the signal, especially in radiometric measurements.

Image Lag
The remain of charges on the PD/ CCD capacity or integrator is called image lag. It causes a virtual subsequent exposure if a dark measurement was done after a light measurement. Especially at CCD's, which came into saturation, several following read out cycles are necessary before the measurement results can be used.

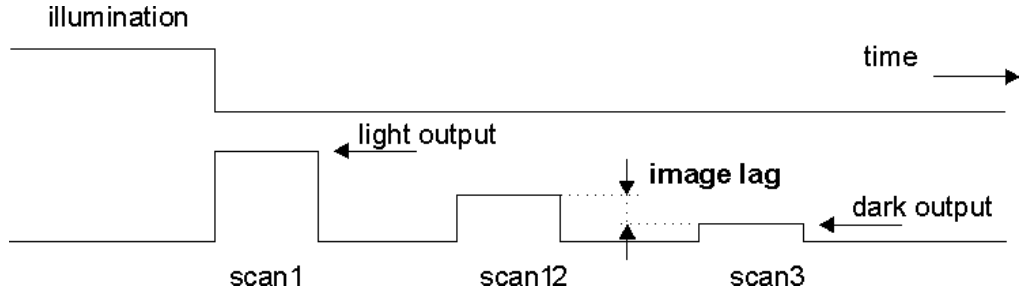


Fig. 15 Scheme of the image lag

2.4 Aspects of Read out Electronics

Types of Video Signals

The classical video signal originates from the TV technologies. The defined voltages are 1 V for the synchronization level, 0.75 V for black and 0 V for white. This video signal is called negative. Furthermore, all video signals have a positive offset voltage shifting the levels to higher values. CCD, like standard types of Sony (ILX series) and Toshiba are designed according to this classic standard.

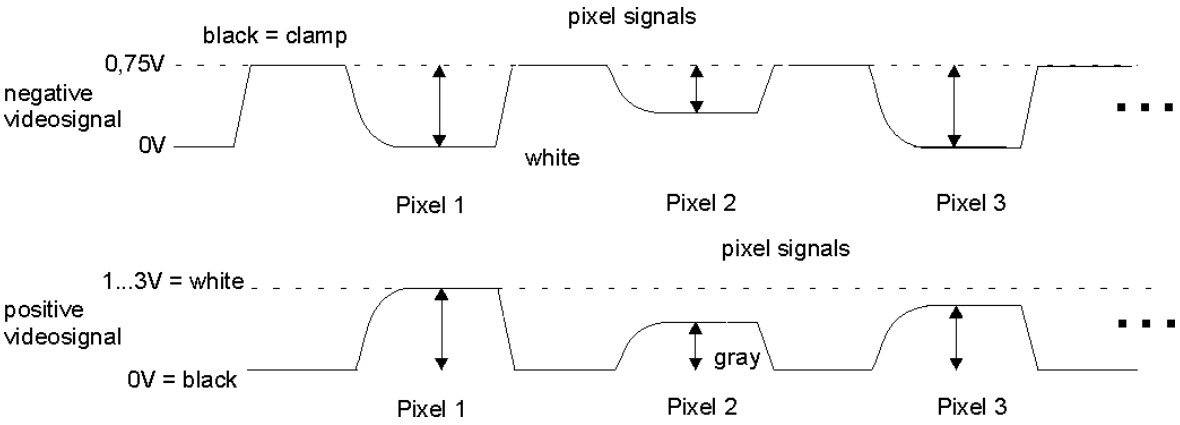


Fig. 16 Diagram of a negative and a positive video signal

Negative video signals often offer a so-called clamp level, which allows to set back the integrator to a defined offset voltage. So it is possible to use the clamp signal for a technique called correlated double sampling (CDS). One capacitor is loaded with the black level, the other one with the active video signal. The combination of both capacitors subtracts the charges. The result is a positive video signal for the ADC. Another solution uses two conversions of the black level and the active video signal and a following difference operation. This solution is much slower than the first one.

The AD conversion is mainly based on a positive ADC related to 0 V. Therefore, a positive video signal offers the advantage of a much simpler subsequent AD converter. Furthermore, an additional noise due to further amplifiers is avoided.

Main arrays, which have the integrator on board, offer a positive signal. Examples are the S837X series of Hamamatsu, the TSL series of TAOS and the arrays of Melexis and IC Haus.

Components of Line Array Read Out Electronics

A read out electronics for line arrays consists of the following main parts:

- Timing: The electronics needs to generate the necessary clock pulses for the array. These pulses differ from array type to type.
- Drive circuit: It serves for the operation of the shift registers.
- Signal processing circuit: It serves for the CDS and the amplification.
- AD converter: It transforms the analog signal to a digital level.
- Processor: It controls all processes and can be used for a precalculation of raw data.

- RAM memory: There can be stored system data (e.g. the pixel – wavelength fit – see chapter 1.2.7. or intensity calibration data - see chapter 3.4.) and measured data (e.g. dark signal or reference signal).
- Interface driver circuits: They manage the data transfer via different interfaces (e.g. USB, RS 232, parallel, CAN).

Reduction of Image Lag

An avoidance or significant reduction of the image lag effect can be reached by a continuous read out of the array, also before the start of the real integration time. JETI's electronic solution applies a fast scan modus, which is used to remove the remaining charge carriers in a short time. A disadvantage of this technique is that the pixels, which are read out first, have a slightly shorter integration time. Another technique is to read out the array continuously. In this case the measurement will be distorted after saturation. The fast scan mode results in a „cleaner" photo capacitor.

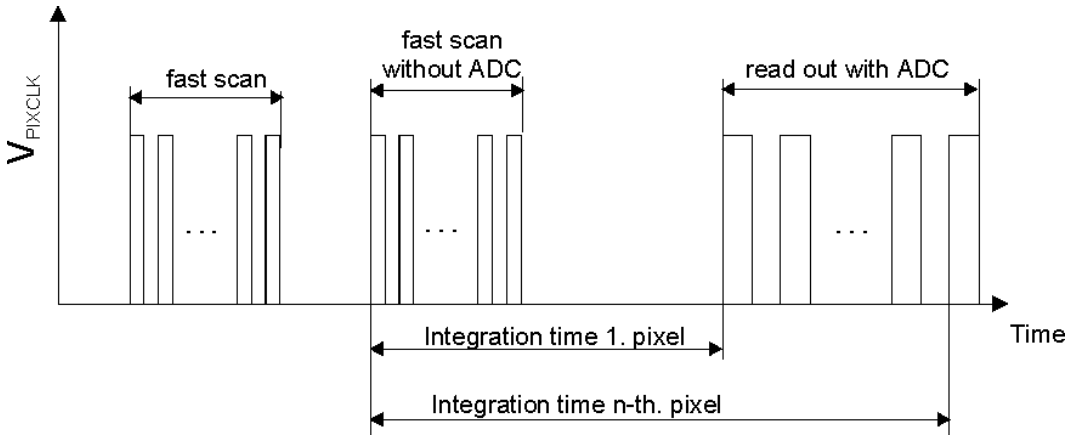


Fig. 17 Read out scheme of a detector array with fast scans

JETI offers several read out electronics for different line arrays. Some types are suited for more than one detector type, e.g. the electronics, shown in the following figure. It is suited for line arrays from Hamamatsu, TAOS, Sony, Reticon, Melexis, Toshiba, iC Haus and Photon Vision Systems.

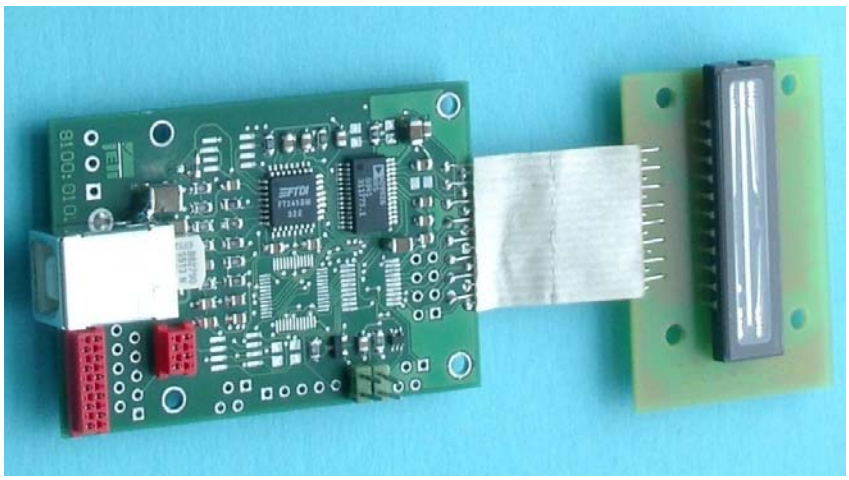


*Fig. 18 Universal controlling electronics **versaspec** for different photodiode and CCD detector arrays example Sony ILX511*

2.5 Examples of Line Detector Array

Producer	Type	Pixel area/ number	Technology	Remarks	Specific features
Hamamatsu	S390x series	50/ 25 µm x 2500/ 500 µm, 128/ 256/ 512	N-MOS (photodiode)	Current output	High UV sensitivity
	S392x series	50/ 25 µm x 2500/ 500 µm, 128/ 256/ 512/ 1024	N-MOS (photodiode)	Voltage output	High UV sensitivity
	S703 x series	24 µm x 24 µm , 512 x 122, 1024 x 122	CCD	Back illuminated	Line binning, high sensitivity (fluoresc. detection)
	S837x series	50/ 25 µm x 2500µm, 128/ 256/ 512/ 1024	N-MOS (photodiode)		High IR sensitivity
Sony	ILX5x1 series	14 µm x 200 µm, 2048 and higher	CCD		Low dynamic range, but high sensitivity
TAOS	TSL140x series	63.5 µm x 55.5 µm, 128	Photodiode		Medium dynamic range
	TSL 1301	85 µm x 77 µm, 102	Photodiode		High sensitivity (fluoresc. detection)
Toshiba	TCD 1201D	14 µm x 200 µm, 2048	CCD		Low dynamic range
Melexis	MLX 90255	66 µm x 200 µm, 128	Photodiode	similar to TSL1401, higher pixels	Integrated charge amplifier
Ret icon	L series	50/ 25 µm x 2500 µm, 128, 256, 512, 1024	CMOS (Photodiode)		
IC Haus	iC-LFF1401	63.5 µm x 56 µm, 128	Photodiode	similar to TSL1401	
Photon Vision Systems	ELIS-1024	7,8 ... 64,4 µm x 125 µm	Photodiode		Electronically selectable pixel number (128/256/512/1024)

3 Selected Applications of Array Spectrometers

Modern array spectrometers as described in chapter 1 find more and more applications in research labs, production and education. Recent developments lead to cheaper spectrometers with improved parameters. One example for the extended application fields are spectral measuring hand held devices. Such instruments were not possible in the past because of the space demanding spectrometer units. Furthermore, there are new light sources available, e.g. UV-LED's, and the read out electronics became smaller and cheaper, even with extended performance.

Selected applications, which are related to different JETI products, are described in the following. These are:

- the color measurement of opaque surfaces
- the photometric and colorimetric measurement of translucent media
- the radiometric and colorimetric measurement of self-luminous samples
- the measurement of fluorescence spectra
- multichannel spectral measurement

The basic rules of color measurement are described in chapter 3.1.

3.1 Color Measurement in General

Color measurement plays an increasing role in quality control of products. Especially the checking of color differences between reference materials and later produced samples is important for the customer acceptance. The easiest way is to observe the samples by the human eye in special cabins, but there arises the problem of objectivity and reproducibility. So color measuring instruments are used, which have to imitate the process of human color perception.

"Let us consider the ´classic island experiment´, in which a random collection of pebbles of all colors are classified by a lonely castaway. Thinking of color in terms of the common names red, blue, green, etc., her first step is to separate those, which have color from those, which have not. In other words, she separates the CROMATIC pebbles from the ACHROMATIC ones. The achromatic pebbles she now arranges from black through gray to white: i.e. she arranges them in order of LIGHTNESS. Turning her attention to the chromatic pebbles, she first separates them into piles of red, yellow, green, etc.: i.e. according to their HUE. Each of these piles she then sorts by lightness in the same way as for the achromatic pebbles. However, she notices that there are still pebbles, which appear different despite being of the same hue and lightness. After some thought, she realizes that this kind of difference relates to how much the colors differ from gray - in crude terms, how much color they contain. This third variable is called CHROMA or SATURATION. Any color can be uniquely specified by the three properties of HUE, LIGHTNESS and SATURATION." (From: Multi-channel detector applications. Andor Technology Ltd. Workshop Belfast October 26-29,1992. p.5).
In technical words: Color is a 3 dimensional quantity. The human eye can distinguish between more than 1 million chromaticity values. Each impression of color for a human being arises from the superposition of the illumination, the reflectivity/ transmittance of the object and the detectivity of the human eye (it contains three kinds of detectors (uvulas) with red, green and blue sensitivity).

Therefore, a color-measuring instrument has to "know" the spectral characteristics of the illumination and of the eye. The latter characteristics are different from person to person, so a standard detectivity was defined by the CIE (Commission International de Eclarage) in 1931 as an average of over 1000 testing persons and is called the normal observer (a new standard is currently under development). It consists of the three standardized uvula sensitivities as shown in fig. 18. They are called values of standard colorimetric observer or color matching functions $\bar{x}$, $\bar{y}$ and $\bar{z}$.

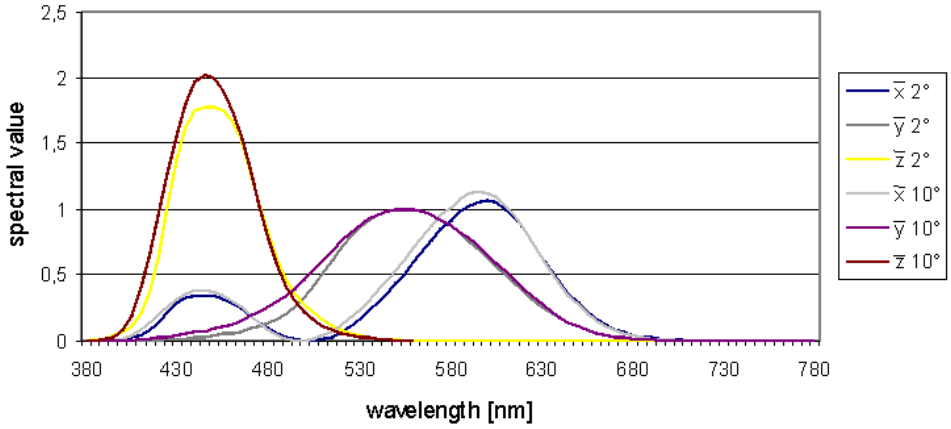


Fig. 1 Functions for the 2° and 10° standard colorimetric observer (available in tables with 5 nm step width, see e.g. DIN 5033/2 or CIE 15.2, data downloadable from: www.hike.te.chiba-u.ac.jp/ikeda/CIE/data/)

It can be seen from the diagram, that the eye sensitivity above 700 nm can be neglected. This is the reason that some color measuring instruments use only the range up to 700 nm.

Color perception is a subjective human observation; this makes the measurement of color very difficult. Influences besides the differing spectral sensitivity of individual persons are the age, the psychological feeling and the surrounding conditions, respectively.

The uvulas are distributed across the cornea with different density, resulting in a changed perception of colors with regard to the illuminated area. The above curves of fig. 12 show two data sets for a narrow viewing angle (2°) and a wider one (10°). The detectivity changes slightly for higher angles, so the characteristics for two observers were defined.

Color measuring instruments can be splitted up into two categories – filter-based and spectrometer-based devices. Filter devices use three special filters, whose transmission characteristics are matched to the three functions of the standard colorimetric observer as precisely as possible. Spectral measuring devices use a spectrometer and therefore have much more detectors with their sensitivity distributed across the VIS spectrum. The standard observer characteristics are used as calculation values, therefore they are more accurate. JETI offers a device of this type with its specbos 4000. The object is illuminated by an internal light source and the signal remitted from the surface under test is measured by a spectrometer.

There exist three different kinds to receive a color impression for the human eye: the color, observed in reflexion, e.g. of a car body (A), the color, observed in transmission, e.g. the colored windows of a church (B) and the color of a light source, e.g. of a light emitting diode (C). Spectral measuring instruments for A are commonly called spectro colorimeters for B spectro photometers devices for C spectro radiometers (see fig. 19).

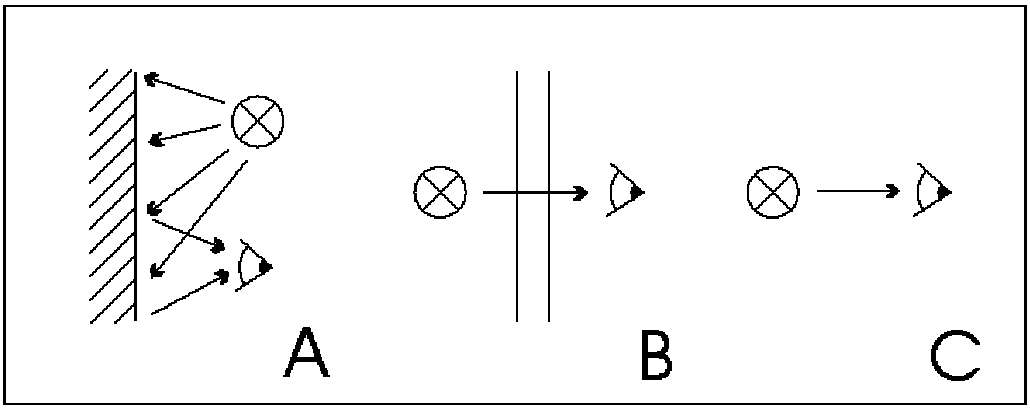


Fig. 2 Kinds of color impression (the physical terms are A – reflexion spectroscopy, B – transmission spectroscopy and C – emission spectroscopy)

Fig. 20 shows a light source illuminating an object, which is observed by the human eye. The illumination spectrum is remitted by the object and therefore weighted with its spectral reflexion behavior. The eye receives this signal and processes it with its own three sensitivity curves. The result is the color impression of the object, expressed by the tristimulus values X, Y and Z.

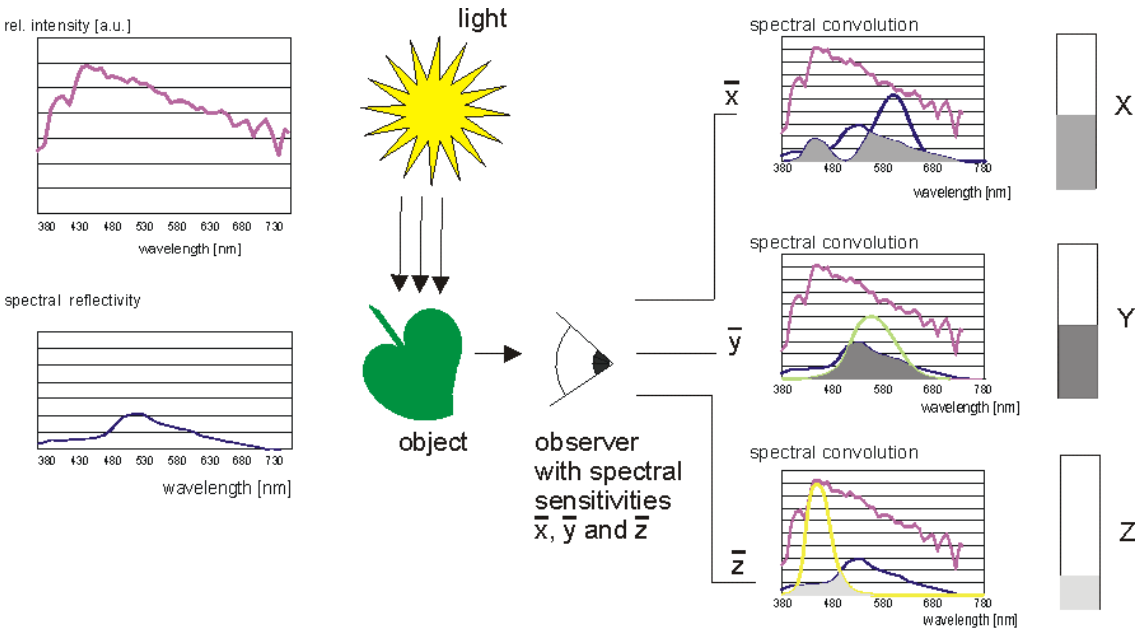


Fig. 3 Object with illuminant and observer

The physical quantity color is a three dimensional value. The following scheme shows the principal calculation process:

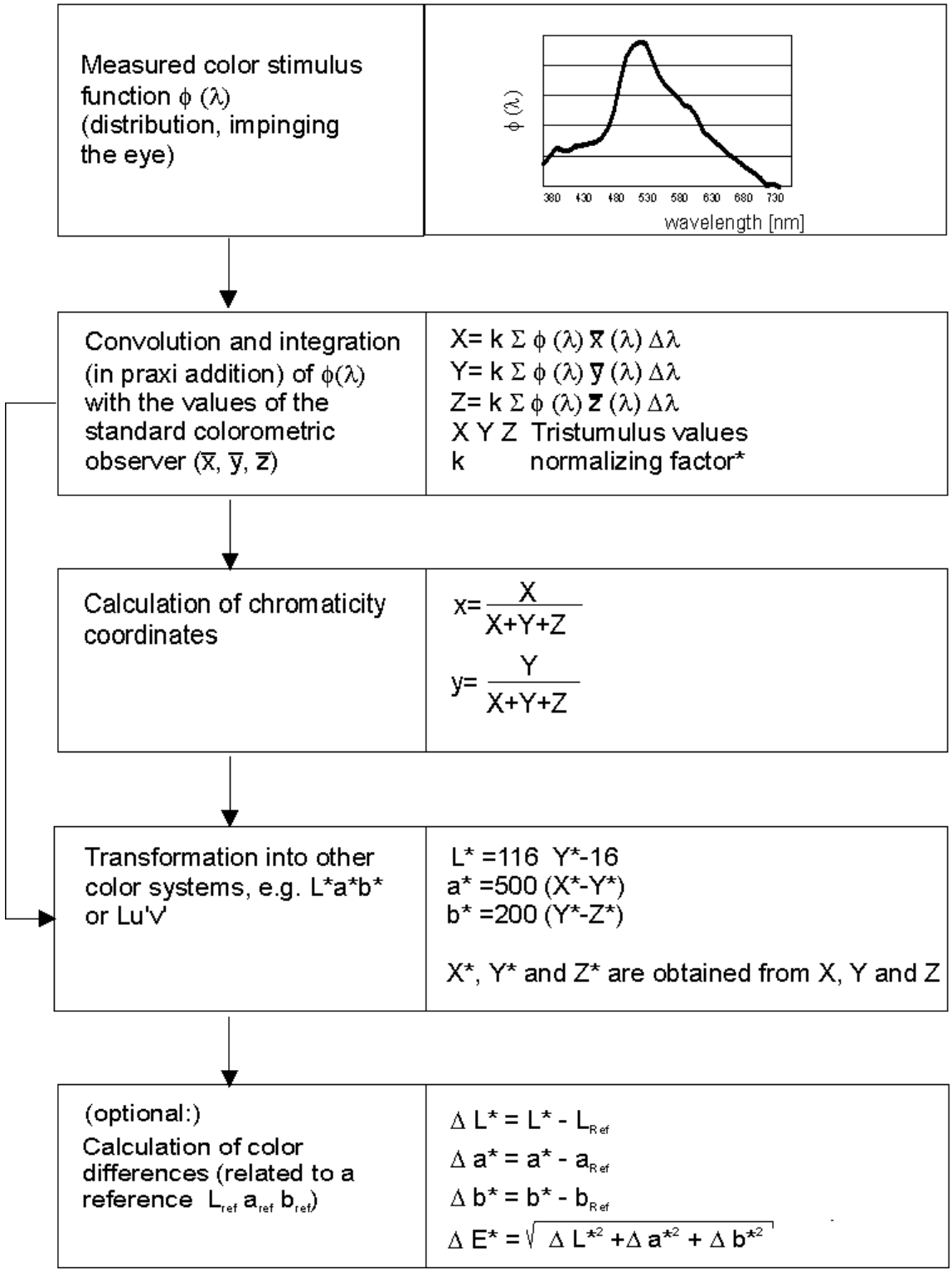


Fig. 4 Procedure of colorimetric calculation (see DIN 5033/2 and /3)
** k is used for the normalization of the tristimulus values like that Y equals 100 for the pure matt white body*

The tristimulus values of X, Y and Z do not offer information about lightness, hue and saturation (see the beginning of this chapter). Therefore, they are transformed into other color systems.
Since the perceived color only depends on the relative amplitudes of X, Y and Z, the chromaticity coordinates x and y are defined as in fig. 21. Additionally z = Z/(X+Y+Z). Because of

$$x + y + z = \frac{(X + Y + Z)}{(X + Y + Z)} = 1 \qquad (10)$$

only x and y are mentioned. These two values do not give information about the intensity; therefore it will be extended by Y. The triple xyY is often used to characterize a color impression.
The x,y diagram has the shape of a sole, the pure wavelengths (spectrum locus) and the so-called purpur line form its boundaries.

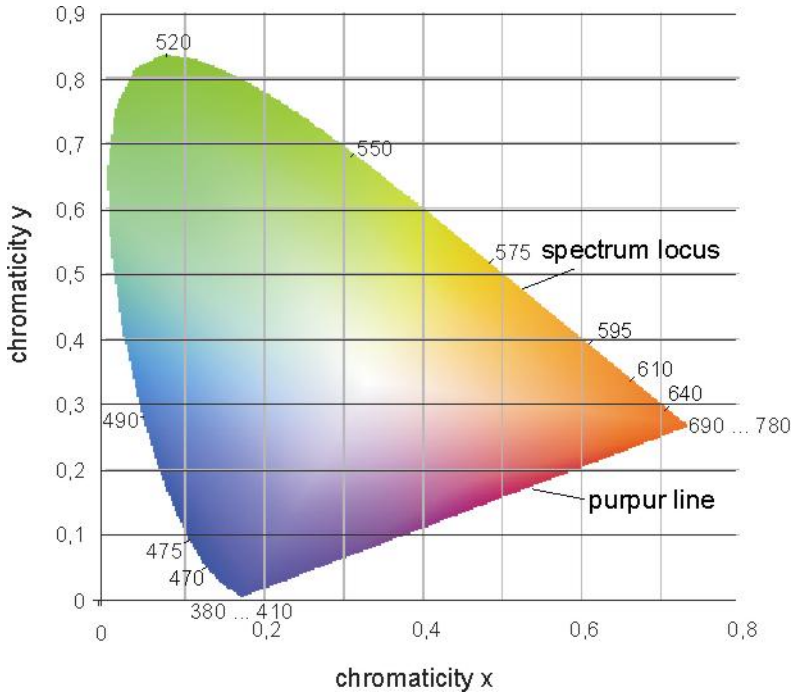


Fig. 5 xy diagram

The intension of color measuring theory during the last decades was to create systems, which are better adapted to the feeling of the human eye. One of the mainly used systems is L*a*b* in which visible color differences (ΔE*) in the whole 3D space are reflected with approximately the same value. The distinction of the asterix values (e.g. Y*) to the values without asterix (e.g. Y) is not indicated in figure 23 for simplicity. The L*a*b* system is better adapted to the subjective color feeling of the human eye than the xyY system.

As mentioned above, a main task of color measuring is color comparison. The geometrical distance of the 3 dimensional color values of reference and sample is used (ΔE*) for easier handling of the measuring results.

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (11)$$

Examples of color measurement can be seen on the demo program JETI specbos color, which can be downloaded from www.jeti.com/Downloads/SD.html.

3.2 Color Measurement of Opaque Surfaces

Colorimetry (Spectral Reflexion Measurement

The color impression of an opaque body is a result of the scattering of the illuminating light on colored pigments in the surface region and the following diffuse escaping of the scattered light. This process is called remission. The remissioned light is influenced by the illumination **and** the illuminated surface (see fig. 20 and 21). Regularly reflected light contains no color information of the reflecting surface.

The measuring geometry, especially the kind of illumination, has a significant influence on the measurement. Two standardized geometries are used for the color impression measurement. The main criterion for the selection of the suited geometry for an application is the kind of the sample surface. Smooth surfaces, e.g. of plastics and varnished materials demand a directed illumination by an angle of 45°, related to the measuring direction. It is preferably arranged cylindrically symmetric around the perpendicular measurement axis. This arrangement avoids the influence of gloss on the measuring result (remember: the regular reflex contains no color information). Rough surfaces, as those of textiles and brickwork, demand a diffuse illumination, obtained by a lamp arranged in an integrating sphere. Two kinds of measurement are possible in this case – gloss included and excluded. The exclusion is obtained by a special gloss trap. The detection of the remission is done directly in both cases. Schemes of both measuring geometries are shown in the following figure:

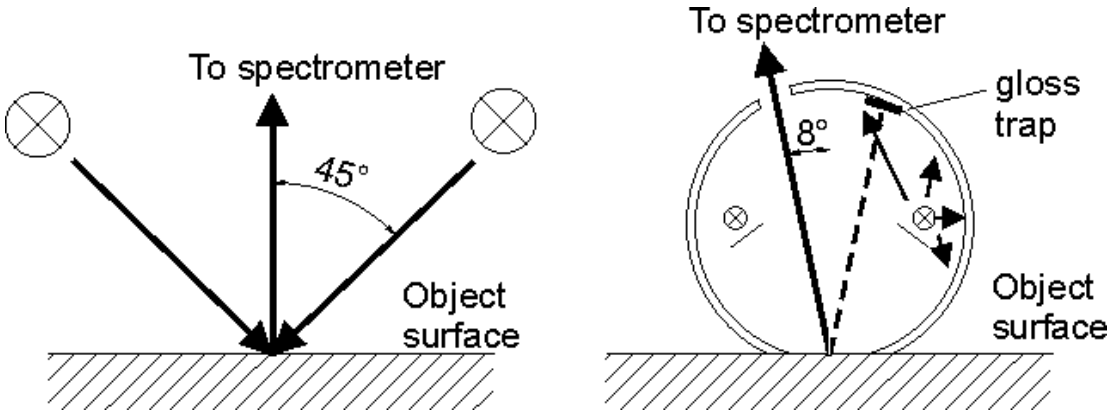


Fig. 6 Both kinds of geometries for reflective measurement of body colors
Left: Directed 45° illumination and 0° measurement (illumination preferably symmetrically) (45°/ 0°)
Right: Diffuse illumination by an integrating sphere and 8° measurement (d/8°)

Light source and detector can be exchanged (Helmholtz reproducibility). This statement is exactly valid only for samples without fluorescence properties. The measuring geometry is described by the specification of the illumination, followed by the specification of the illumination, followed by the specification of the observation path (according to ASTM and CIE).
The specbos 4000 of JETI has a fiberoptic 45°/ 0° measuring geometry. Its measuring head has to be placed in direct contact to the object under test.
The results of a color measurement are strongly influenced by the details of the used measuring geometry, e.g. by the aperture of illuminant and detector. This is the reason for different results obtained by different instruments, especially if different manufacturers design them. The main criterion of an instrument is the comparability between devices of the same type – the device intercomparability.
As outlined in the general chapter about color measurement the color impression of an object is dependent on the illumination spectrum and on the colorimetric observer. To obtain comparable measuring results the observer (see fig. 18) as well as the illumination (e.g. daylight or the light of an incandescent lamp under specified conditions, see fig. 24) are standardized. Every measuring result has to include the related measuring conditions.
It is not possible to obtain a standardized illumination spectrum in an ideal way for measuring purposes, but if the special illumination spectrum of the measuring device is known, it can be mathematically converted into such standardized characteristics.
The calculation of the color values is proceeded according to the scheme of fig. 21. The only addition is that the measured spectrum $\varphi(\lambda)$ is the product of the standard illuminating spectrum S_λ, which shall be used as reference for the color coordinates, and the spectral reflexion coefficient (spectral density) of the sample $R(\lambda)$

$$\varphi(\lambda) = S_\lambda \cdot R(\lambda) \qquad (12)$$

The sample spectral density is determined by the ratio of the spectrum measured with the sample to the spectrum measured with a white standard of known spectral reflectivity. Therefore, it is not necessary to illuminate with a standard illumination.

$$R(\lambda) = \frac{I_{sample}(\lambda)}{I_{ref}(\lambda)} \qquad (13),$$

with $I_{sample}(\lambda)$ the measured spectrum with the sample and $I_{ref}(\lambda)$ the measured spectrum with the reference standard. It is a fundamental condition for this measurement that the instrument illuminant spectrum is kept constant during the measuring period (measurement of standard and of sample), if no referencing is used.
The instrument illumination spectrum can have an arbitrary distribution, but has to include all parts of the visible range from 380 to 760 nm or at least from 400 to 700 nm. Best results are obtained by a homogeneous distribution across the spectrum due to an equal dynamics.

Fig. 25 shows two different standardized illuminations, which are often used. Several more spectra, as daylight of other color temperatures, artificial daylight, Xe lamp light, etc. are defined (see DIN 5033/7).

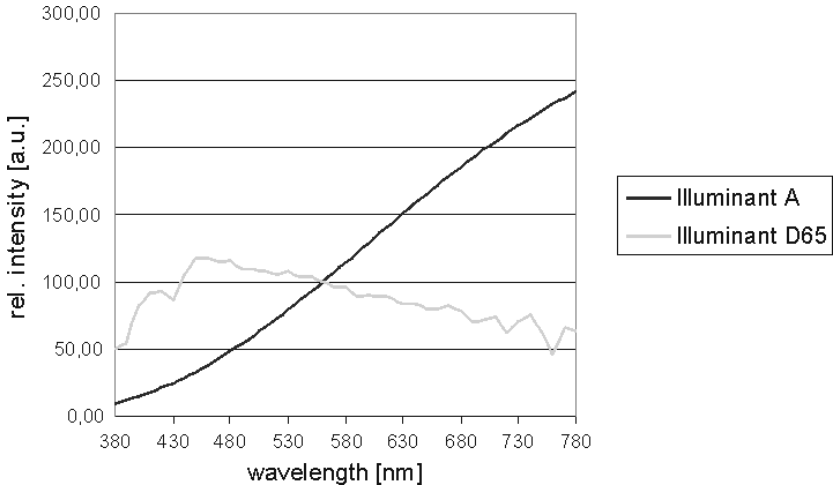


Fig. 7 Standardized spectra D65 (daylight with a color temperature of 6500 K) and A (incandescent lamp)

Two samples with different remission (or transmission) spectra, which give the same color values with one illuminant, mainly show different color values for other illuminants. This effect is called metamery. The value characterizing this behavior, is the metamery index. It describes the color difference of the samples measured at a specified illuminant and related to the reference illuminant where the color difference is zero.
Every body color measurement instrument is delivered with at least one reference standard. This standard, a white sample, has to be traceable to measurements of a standardization institute. It is used for calibration of the instrument before a measurement series to know the instrument illuminant spectrum $I_{ref}(\lambda)$. So the measuring results are fitted to this normal and internal effects of the instrument (as degradation of the light source) are excluded.

Fig. 8 Colorimeter specbos 4000 with calibration standard

3.3 Photometric and Color Measurement of Transmittive Samples

Spectralphotometry (Transmission Measurement of Liquids, Filters and Transparencies)

Modern spectrophotometers, for instance the specbos 3000 of JETI, are easy to use instruments for non-destructive testing in many application fields. They basically consist of a regulated light source with collimation optics, a test cell holder, a focusing optics, a spectrometer, the read out electronics and a microprocessor for data management and calculations.

Fig. 9 Spectral photometer specbos 3000

The basic measurement of a spectrophotometer is the determination of the spectral transmission of the sample according to the following formula:

$$\tau(\lambda) = \frac{I_{sample}(\lambda)}{I_{ref}(\lambda)} \cdot 100\% \qquad (14)$$

$I_{sample}(\lambda)$ and $I_{ref}(\lambda)$ are the measured intensities with sample and with reference at the different wavelengths λ. The unit of $\tau(\lambda)$ is % or 1. Several application fields prefer to use the logarithmical expression of absorbance according to the formula

$$A(\lambda) = -\log \frac{I_{sample}(\lambda)}{I_{ref}(\lambda)} = -\log \tau(\lambda) \qquad (15)$$

The unit of absorbance is AU (absorbance units). Other physical terms with the same meaning of absorbance are extinction or optical density.

The main interest of a user in analysis is the concentration of a sample. So it is necessary to implement the calibration of the concentration – absorbance relationship into the instrument.

3.3.1 Optical Parameters

The main parameters of a spectrophotometer are:

- wavelength range
- optical resolution
- wavelength accuracy
- wavelength precision
- photometric linearity
- photometric precision
- photometric accuracy
- stray light

In the following there is given an overview of the meaning and test of these quantities. The issues of wavelength range, optical resolution and stray light are treated in the general section (see chapter 1.2. Spectrometer Parameter).

Wavelength Accuracy and Precision

The primary wavelength calibration of a spectrophotometer can be done in two different ways:

- Transmission measurement of media with strong absorption bands of well-known wavelengths
  Commonly used liquids for UV and VIS are solutions of Holmium Oxide and Samarium perchlorate. They are available in permanently sealed cells. More convenient standards are filter glasses with strong absorption bands (Didymium = Neodymium and Praseodymium or Holmium glass). Examples for theses glasses are BG 36 and BG 20 (Schott). The latter has absorption bands at 528.7 and 684.3 nm, which are used for the calibration test of the specbos 3000.
- Emission measurement of a line lamp (e.g. low pressure Hg in VIS)
  During this calibration only the detecting part of the photometer (the spectrometer with input optics) is used. The spectral peaks of the lamp are applied for the calibration see chapter 1.2.7.).

The wavelength-pixel relation is given as a polynom as described in the general section.
Wavelength accuracy is the deviation of the average wavelength reading at an absorption or emission band from the known wavelength of this band, while precision means the ability of a spectrophotometer to reproduce the measured wavelengths. The test measurement procedures are described in the Standard Practice E 275 of ASTM (available from www.astm.org).

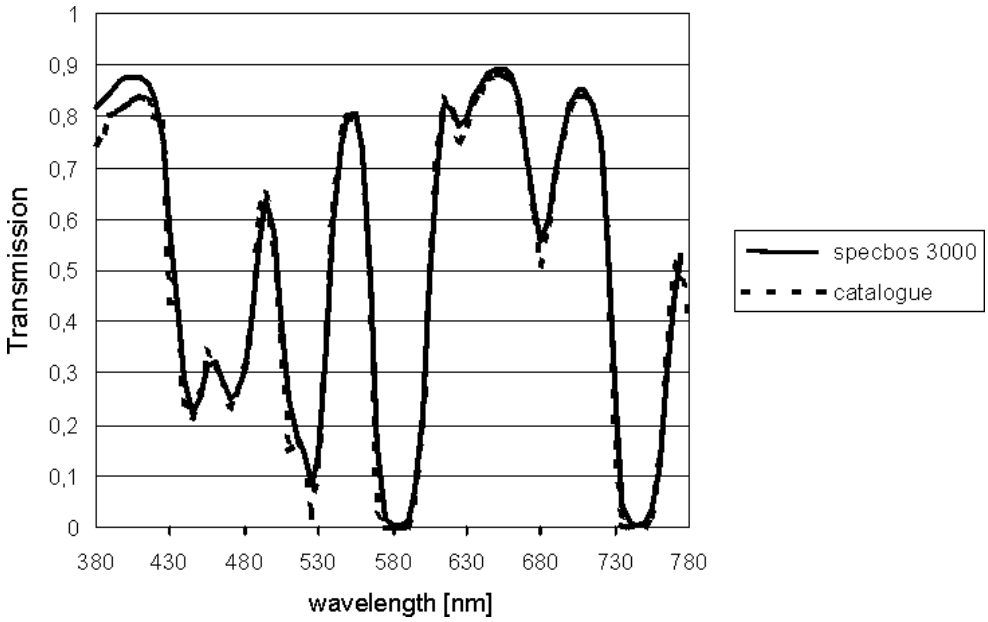


Fig. 10 Transmission spectrum of a Schott filter BG 36, thickness 1 mm

Photometric Linearity

It is important to know the range of linearity for the absorbance measurement, and therefore, in case of analytics the range for a correct concentration measurement. Potassium dichromate solutions of different concentrations are commonly used as photometric linearity standard in the UV range. For the VIS range neutral density filters of different absorbances (e.g. between 0.2 .... 2.5 AU) are used. They are more practicable and stable, but less precise and more scratch sensitive. With these standards the determination of the linearity is possible by plotting the measured absorbance against the known one. Details can be obtained from the above-mentioned ASTM practice.

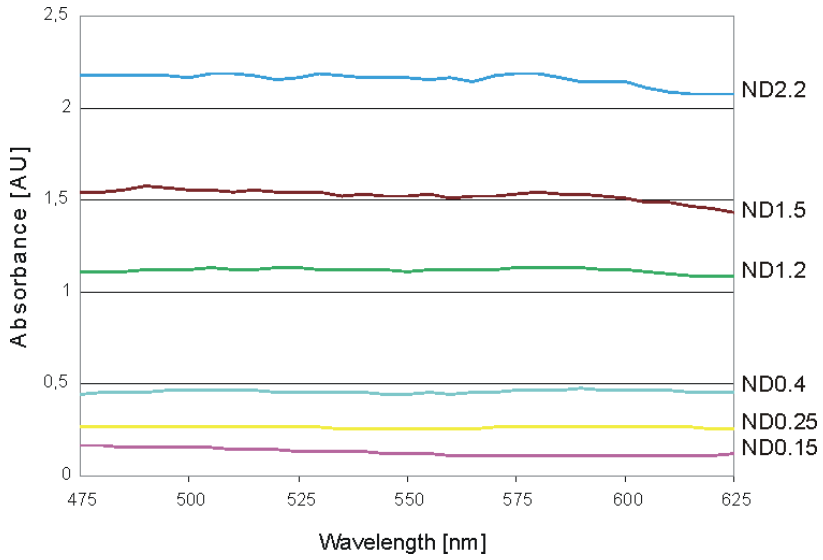


Fig. 11 Diagram with different ND filters, useable for photometric linearity measurement

The following diagram shows a typical result of such a measurement.

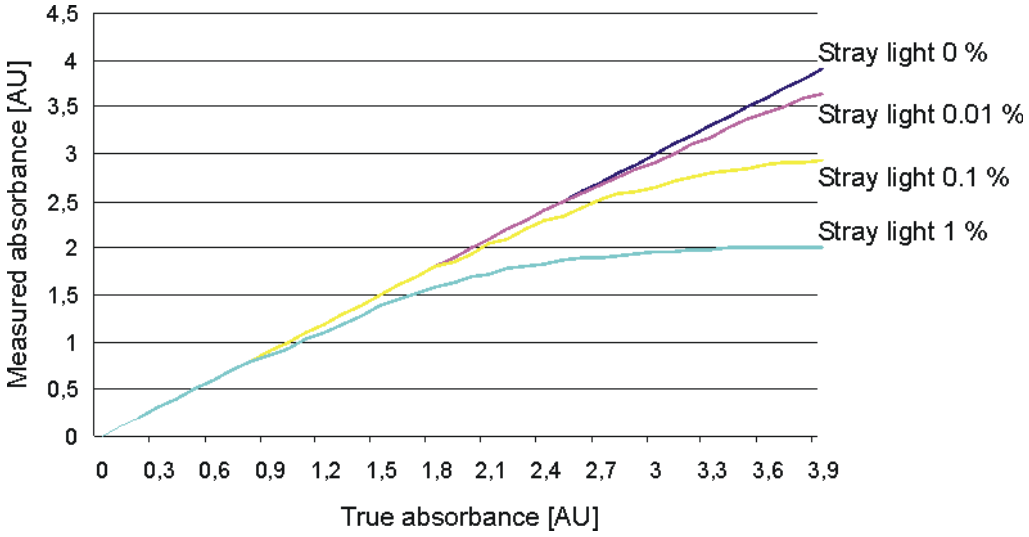


Fig. 12 Photometric linearity of a spectro photometer

It can be seen that the range of linearity is strongly influenced by the stray light behavior of the spectrometer. The lower the stray light the broader is the absorbance range, which can be used for a precise measurement.

Photometric Precision
It represents the ability of the photometer to reproduce the result in successive measurements. The parameter for the photometric precision is the standard deviation. The value is determined by at least ten transmission measurements of ND absorbance filters or perforated screens of defined absorbance, followed by the standard deviation calculation.

Photometric Accuracy
Sometimes, not in all applications, the accuracy of the photometric measurement is of interest, e.g. if absorption measurements of different labs have to be compared. The accuracy gets determined with transmission samples, which are traceable to national standard laboratories, e.g. NIST standard reference materials. The accuracy is the difference between the true absorbance/ transmittance values and the average of ten measured values.

3.3.2 Measuring Geometry

The measuring geometry with transmission of a collimated beam through the test sample, as described in the beginning of this chapter is only useful for samples with low scattering, e.g. colored liquids or colored glasses (0°/0° geometry). In case of higher scattering media, such as milk or filters with a rough surface, it is necessary to use a diffuse illumination by means of a lamp in an integrating sphere and leaving the detection path with a focusing optics (d/ 0° geometry). Again it is possible to exchange illumination and detection path. A 0°/ 90° measuring geometry is used for fluorescence applications to reduce the influence of the exciting beam (see chapter 3.5.).

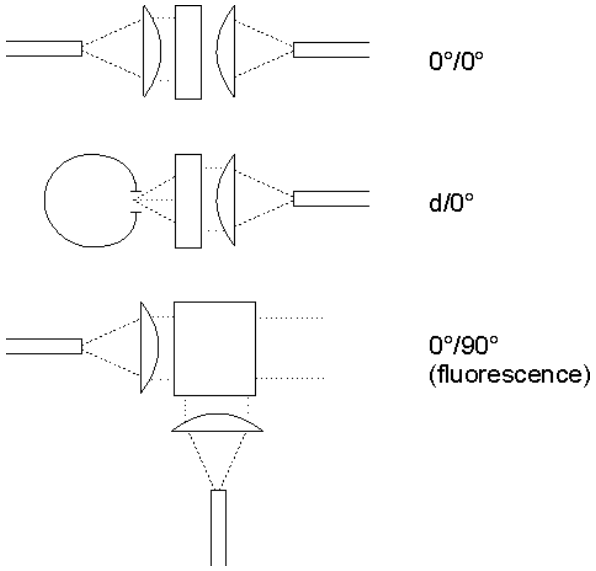


Fig. 13 Set-ups for transmission and fluorescence measurement

Liquids are normally measured in test cells. There are several kinds on the market: round and rectangular, made from plastics (non-returnable), optical glass, Spectrosil quartz and UV silica. The standard width is 12.5 mm and the optical path length can vary between 1 and approx. 100 mm. The standard path length is 10 mm. A very important point is the z height dimension, this is the distance from the bottom of the cell holder to the center of the incident light beam (standard values are 8.5 or 15 mm, JETI´s specbos 3000 uses 15 mm). The z height becomes very important when the aperture of the cell is small. For continuous (online) measurements flow cells with liquid in and output are used.
If test cells are used, the sample of the liquid under test has to be brought to the instrument. This procedure is not convenient for several applications, e.g. in process control. In this case dip probes are used, which are inserted into the test liquid to proceed in situ measurements. Such probes are mainly fiber coupled.
JETIs specbos 3100 is an example for an instrument with dip probe. It has a fiberoptic output connector for the illumination and an input guiding the signal to the spectrometer. The dip probe (see Fig. 31) consists of two fibers, which are linked to these connectors. It furthermore consists of a collimating optics, a protective window and a mirror with protective layer, housed in a stainless steel tube. The illumination light, escaping from one fiber, gets collimated, transfers the distance from the window to the mirrow and backwards, until it is focused into the second fiber. The optical path length (measuring length) is the double window – mirror distance (in most of the cases). There are dip probes with fixed (e.g. 1 mm, 2 mm, 5 mm) as well as with variable path length on the market. There exist several mounting technologies to protect diffusion of test liquid into the probe, these technologies have strong influence on the price of the probe (e.g. glued, sealed with O rings or connected by diffusion welding). Furthermore, the surrounding conditions can be very different (e.g. temperature, pH factor, pressure), so it has to be checked carefully whether a probe is suited for a certain application or not.

The influence of a possible fiber movement lies in the 1.. 3 % range, therefore it is recommended to fix the fibers before proceeding the measurement.

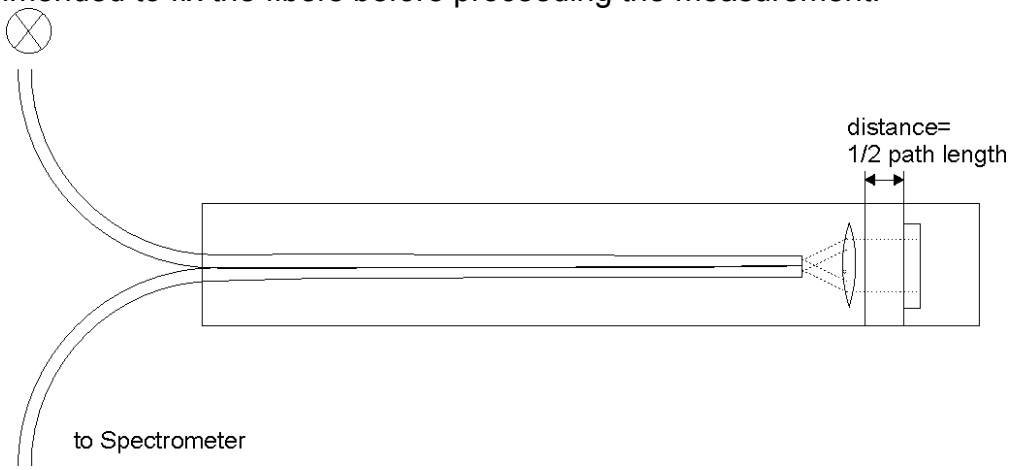


Fig. 14 Fiberoptic dip probe

3.3.3 Color measurement

The color measurement of transmissive media, e.g. liquids or transparent solid media (color filters, transparencies), has the same physical background as described for the reflectance measurement. The illumination can be diffuse or directed and is usually of the C type. The observation is normally under 0° on the opposite side of the sample (standard EN 1557). The calculation procedure is the same as in case of reflexion measurement. Therefore, the JETI spectrophotometer specbos 3000, normally delivered with a spectral measuring software, can be used with the color measuring software JETI specbos color for such applications. The only difference is that an aqua dest. filled test cell or an uncolored sheet of material is used as the reference standard. The spectrum of this reference is set to 100 % for the whole wavelength range or a traceable spectral transmission across the wavelength range of interest is available. The simplification with the 100 % reference is especially useful in applications with color comparison only.
In former times, the color determination of liquids was based on a comparison with master solutions. Based on this, several color scales depending on the concentration were created for different application fields.
There are the following examples:

- Iod number – describes the color depth of clear liquids as solvents, softening agents, resins, oil (DIN 6062)
- Hazen number – characterization of roughly water clear liquids, especially with pale yellow color (ISO 6271)
- Gardner – used for pale yellow samples, e.g. fat (ISO 4630)
- Lovibond number – originally for beer mash characterization, today used in fat and oil industry (AOCS Cc 13e)
- Seyboldt number – water clear to pale yellow liquids (for pharmaceutical white oil, paraffin and mineral oil, ASTM D 156)
- Klett number – photometrical value for cosmetics industry

These numbers are only valid for the same and similar chromaticities. Such color measuring numbers were defined empirically. Today these color scales are implemented in the software of spectrophotometers, so it is easy to use the instruments in different industrial fields. The following figure shows the Iod, Hazen and Gardner color numbers in the chromaticity diagram for specific test conditions.

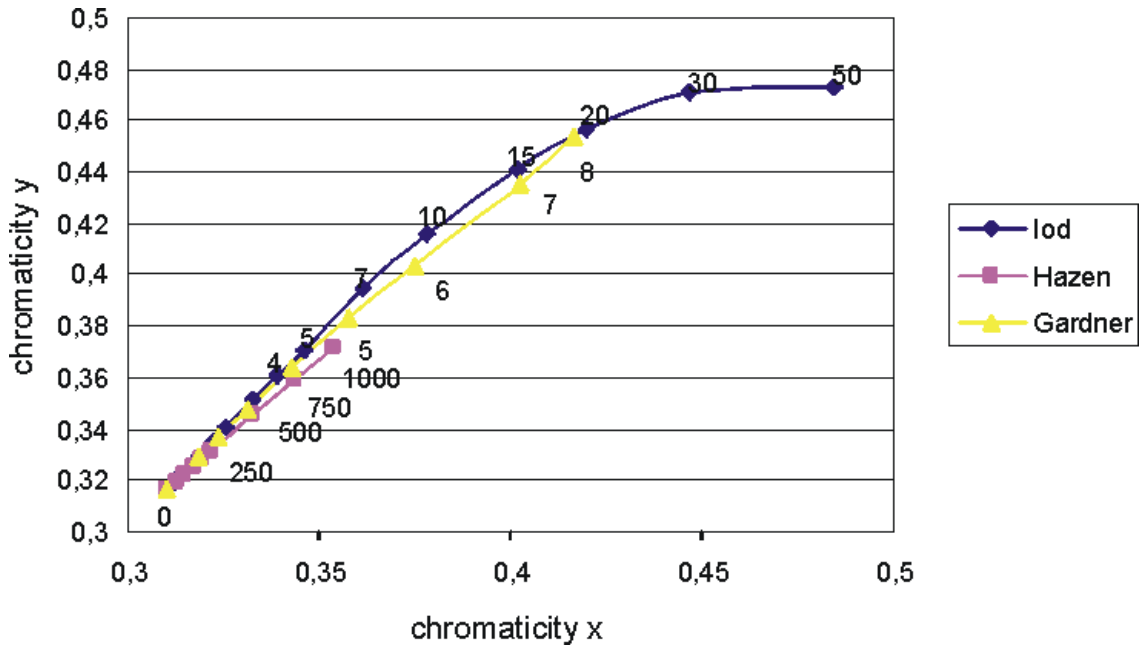


Fig. 15 Iod, Hazen and Garner color numbers in the chromaticity diagram (standard illuminant C, 2° observer, test cell thickness 10 mm) From: Standard EN 1557

3.4 Measurement of Self-luminous Objects

Spectroradiometry

For the color measurement of light sources like CRT´s and illuminated areas like projection screens again filter as well as spectrometer based instruments are used. The calculation of color values is based on the same rules as described in the general chapter. In contradiction to body color, there are only light source (in this case as object) and observer (detector) necessary (see fig. 19 C).

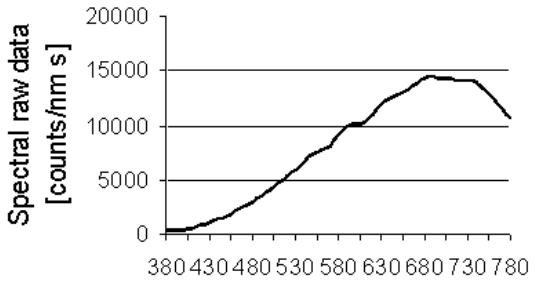
Therefore, equation (12) will be replaced by

$$\varphi(\lambda) = S(\lambda) \qquad (16)$$

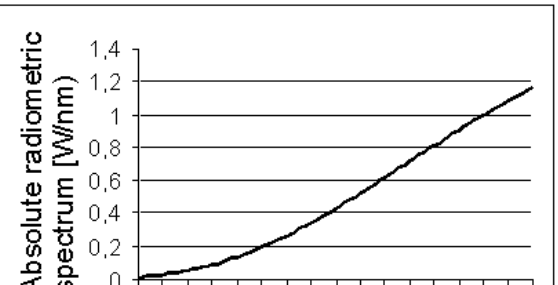
where S(λ) is the spectral power distribution of the light source under test.
Normally, spectroradiometers have a field of view between 1 and 3° to obtain a small measuring diameter. The measured radiation is focused onto the input of a spectrometer by a lens or a lens system. The spectrum is used for the calculation of quantities as radiance, luminance, chromaticity and correlated color temperature according to the following scheme:

Measurement of light source spectrum $S(\lambda)$ [$\frac{counts}{nm}$]

(at suitable integration time) t_{int} → relative spectrum[counts/ nm s]



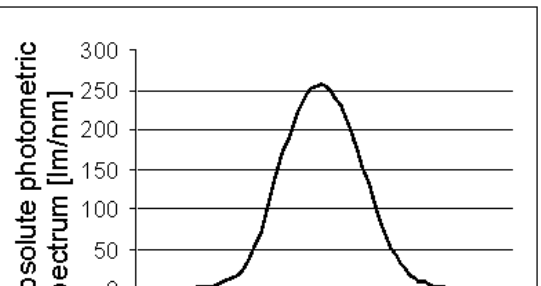
Division by spectral sensitivity of the measuring system[counts/Ws]
→ absolute spectrum S_{abs} (λ) [W/ nm]



Integration (addition)
→ integral physical value

- related to viewing angle and light source area → **radiance**
- related to illuminated area → **irradiance**

Convolution with luminous efficiency function($v(\lambda)$)
→ absolute photometric spectrum



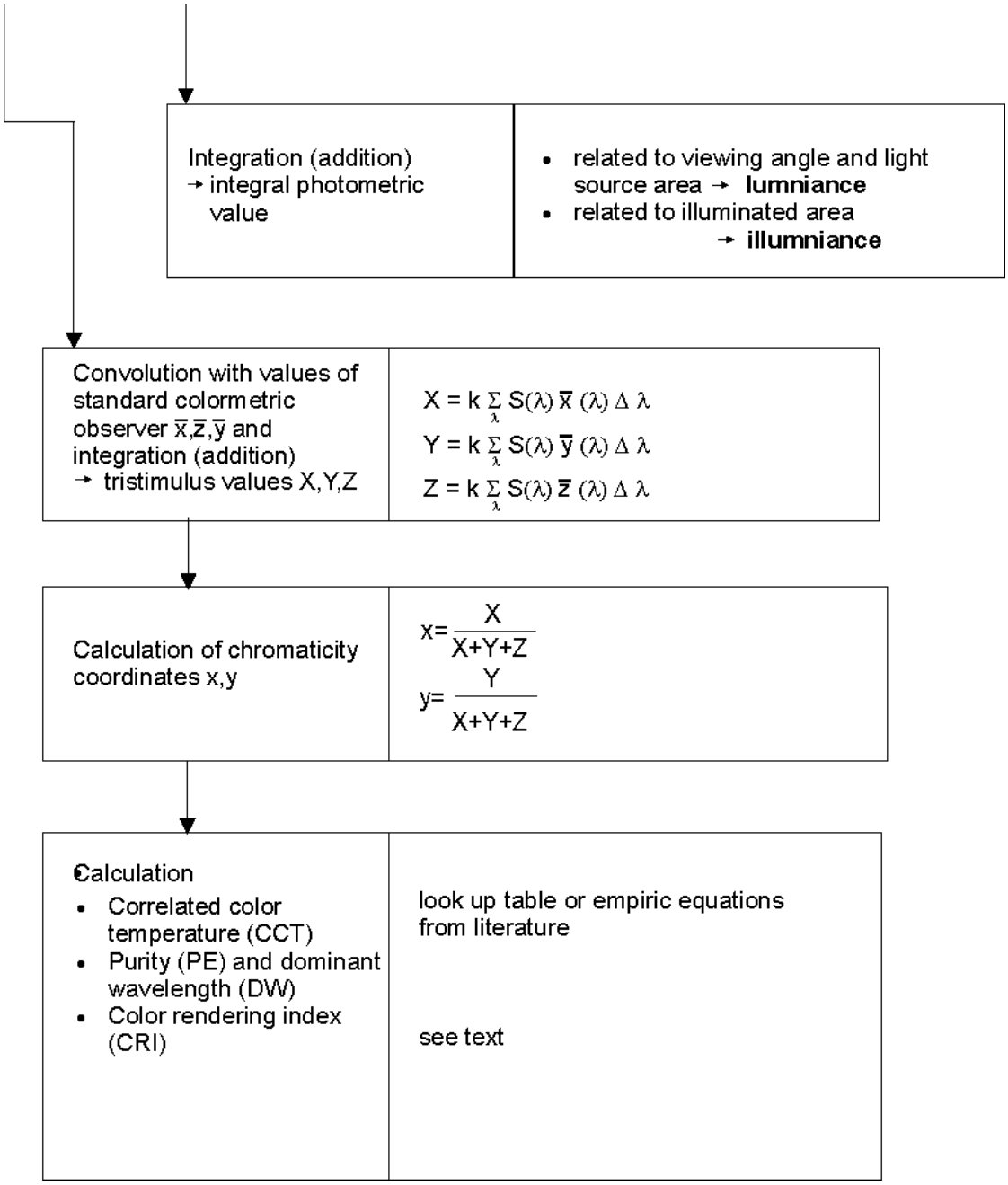


Fig. 16 Scheme of spectroradiometric calculation

It can be seen from the second step that it is necessary to calibrate the spectrometer intensity axis for spectroradiometric measurements to know the sensitivity of the system. In case of a body color-measuring device it is simply done with a white reflexion standard, which is delivered with the instrument. The manufacturer or supplier of the instrument normally does the calibration of a spectroradiometer. Halogen lamps with an integrating sphere (luminance standards) and standard lamps for luminous intensity are mainly used. The recalibration of the instrument is necessary and normally recommended once a year.

Fig. 17 Spectroradiometer specbos 1200

The color measuring values are the same as at body colors, in particular the chromaticity values x y or u´v´ are used. Another kind of description for a position in the chromaticity diagram is a combination of dominant wavelength and color purity. The following figure shows the determination of both values.

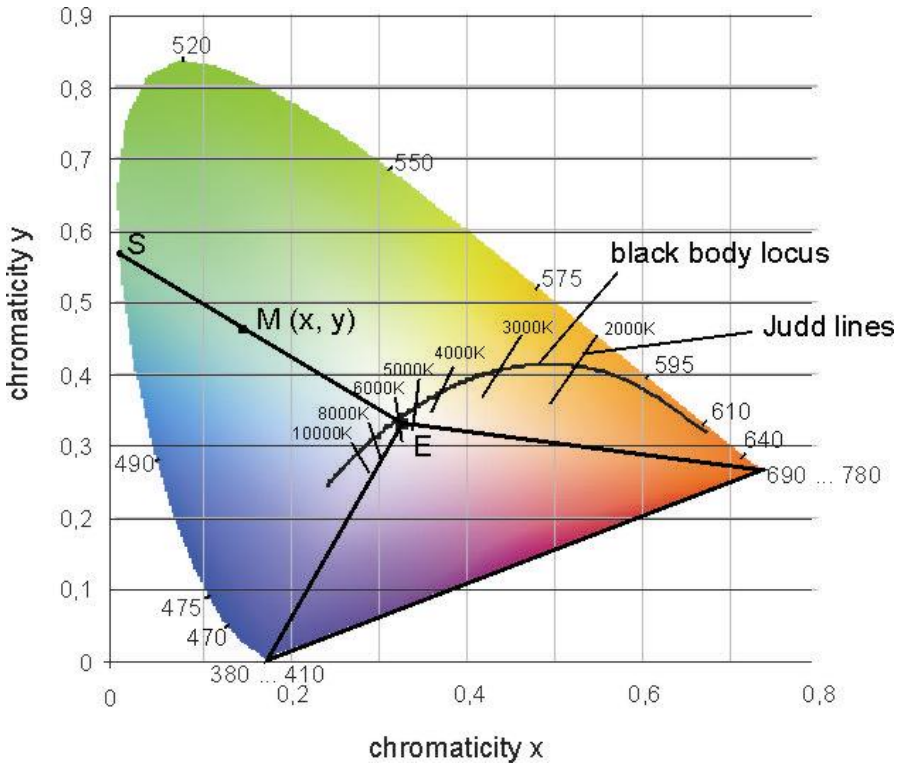


Fig. 18 Chromaticity diagram with indication of the dominant wavelength/ color purity definition and the blackbody locus with Judd lines

The **dominant wavelength** is determined by the extension of the connecting line between the location of the equi-energy spectrum E (x = 0.333, y = 0.333) and the location of the measured chromaticity M (x,y) to the outer border of the diagram,

the spectrum locus. The wavelength of this point of intersection S is the dominant wavelength (DW). The ratio between the distance EM to the distance ES indicates the **color purity** (PE). The more narrow the spectrum, the higher is the color purity. Monochromatic sources have a value of 100 %. The locations on the purpur line have no assigned wavelengths. If the measured color point M lies inside the triangle 380 nm – E – 780 nm, than the extension is made from M beyond E to the intersection with the spectral locus. The resulting wavelength is indicated by a negative sign and called the complementary wavelength.

A further parameter of light sources is the **Correlated Color Temperature** (CCT). The chromaticities of black and gray bodies with different temperatures lie on the blackbody locus in the chromaticity diagram (see fig. 36). This statement is only in rare cases exactly valid for other spectra. Nevertheless, the color temperature is an advantageous and simple indication. For chromaticities near the blackbody locus it is common to give the temperature of the gray body which chromaticity is nearest to that of the concerning light source. This is the Correlated Color Temperature (CCT). The CCT tells nothing about the spectrum of the light source under test. It is the temperature of the blackbody radiator when the color appearance is the same as the source being tested. So it is not a measurement of the physical temperature of the light source.

The connecting lines of the chromaticity locations with the same CCT are called Judd lines. The bigger the distance between a color point and the blackbody locus the higher is the uncertainty of the CCT. If it is too far away, the information will become senseless.

The transformation from the chromaticity coordinates to the CCT can be done by look up tables or, as in case of the JETI spectroradiometer specbos 1100, by approximation with empirical formula.

The **Color Rendering Index** (CRI) is a calculation value to specify the color rendering properties of light sources, based on a test color sample method. It indicates the color differences of defined (theoretical) samples, illuminated by the lamp under test and a reference illuminant. 14 samples are defined by their spectral radiance factors, 8 of them are selected to cover the hue circle, but moderate in saturation and approximately the same in lightness and the other six representing a strong red, yellow, green and blue as well as complexion and follage colors (vary widely in color). CRI is always related to a certain reference illuminant, which has to be indicated.
The first step of CRI calculation is to determine the set of tristimulus values X, Y and Z, resulting from the illumination of the defined samples by the light source under test and the reference illuminant (see fig. 22). Then the corresponding chromaticity values u and v are calculated, followed by a correction for the adaptive color shift due to the different state of chromatic adaptation under the lamp to be tested and under the reference illuminant. After transformation of all color data into special uniform space coordinates the color differences ΔE_i for all samples, illuminated with both illuminants, are calculated.

The special CRI is given by a set of R_i according to the formula

$$R_i = 100 - 4.6 \cdot \Delta E_i \quad \text{with i= 1 ... 14} \qquad (17),$$

whereas the general CRI is the arithmetical means of the eight special CRI for the test samples 1 ... 8 (see CIE publication 13.3 – 1995, www.cie.co.at).
Furthermore, from the absolute spectral data of light sources integral intensity data can be calculated. The selection of the proper lighttechnic value depends on the kind of light source. E.g. the „intensity“ of a LED detected by the human eye is given as luminous flux (cd), whereas homogeneous sources as CRT screens are specified by their luminance (cd/m²). The following figure shows the suited measurement set-ups for different kinds of light sources.

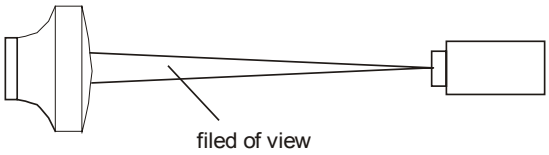
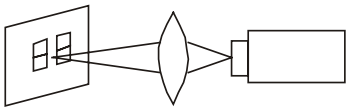
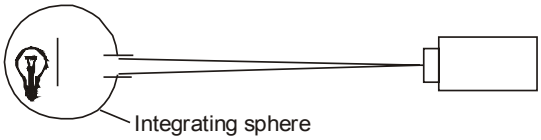
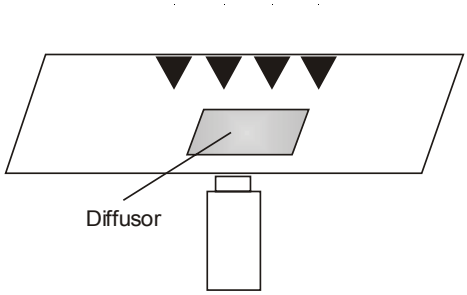
Object	Measurement set-up	Measurement Value
Screen, displays		**Luminance** $[\frac{cd}{m^2}]$
Segments of displays		**Luminance** $[\frac{cd}{m^2}]$
Directed bright light source (reflector lamps, lensed lamps, LED)		**Luminious intensity** [cd]=[$\frac{lm}{sr}$]
Total radiation of diffuse light sources (bulbs, fluorescence lamps)		**Luminious flux** [lm]
Illuminated areas (work place), digital projectors		**Illuminance** [lx]=[$\frac{lm}{m^2}$]

Fig. 19 Measurement set-ups for different kinds of light sources

As stated before, it is necessary for all absolute intensity measurements to calibrate the intensity axis of the spectrometer. This can be done by means of a lamp in an integrating sphere, whose spectral power data at the output hole are known. The field of view of the spectroradiometer will be precisely directed into the hole of the sphere in case of luminance measurement. For illuminance measurement the spectroradiometer gets a diffusor in front of the optics to create a cosine detection behavior. The calibration can be done with a light source of known luminous flux (e.g. incandescent lamp) or luminance (incandescent lamp in integrating sphere) and corresponding conversion into irradiance/ illuminance.

Spectroradiometers (luminance as well as illuminance meters) are classified according to definitions to be found in standards (DIN 5032/6 and /7 as well as CIE publication 69). Several measuring errors, e.g. the deviation from the $v(\lambda)$ function, the deviation in directional response, the effect of polarized light, the linearity deviation, etc. and the maximum ranges of the errors are fixed in these papers. The instruments are classified into four categories from highest (class L) to lower precision (class C).

3.5 Spectral Fluorescence Measurement

Photo luminescence is the property of a substance or body to absorb light of a certain wavelength and emit at a higher wavelength with lower energy and slightly later. The difference between the exciting and the emitted wavelength is called Stokes shift. If the process duration lies in the µs or ns range, it is called fluorescence, in case of a longer time delay between excitation and emission it is called phosphorescence.
Common applications of fluorescent materials are:

- Characteristic features against counterfeites bank notes and stamps
- Luminous layers in CRT
- Endangering signs
- Optical brightening agents for paper, textiles and polymers
- Analytical applications

The application of such materials makes it necessary to measure their spectral behavior, e.g. for quality control purposes.

If the reflexion or transmission spectra of non fluorescent media are measured with a scanning monochromator systems (sequential excitation by several wavelengths and integral measurement) and line array spectrometers (parallel measurement), the results are the same. In case of fluorescent materials the spectra differ. The reflexion/ transmission spectra of a scanning system do not exceed the 100 % line, because absorption and (fluorescence) emission are registered combined. If a line array spectrometer (polychromator) with integral illumination across the whole wavelength range is used, the absorption and emission behavior is shown correctly. There are regions where the spectrum exceeds the 100 % line due to fluorescence emission and simultaneous illumination at the lower excitation wavelength.

The scheme of a spectral fluorescence measuring system is shown in the following figure. An excitation monochromator is tuned to the absorption band of the material to be measured, which almost equals the region with most effective fluorescence excitation. This monochromator can be replaced by a monochromatic light source (laser or LED with a short pass filter) in case of applications where the wavelength flexibility is not necessary and the sample is always the same (e.g. in check of characteristic features against counterfeiting). This solution offers the possibility of economic systems for QC processes in the production. The sample is illuminated in reflexion or transmission. A polychromator measures the fluorescence signal over the full wavelength range. So it is possible to detect different fluorescence peaks.

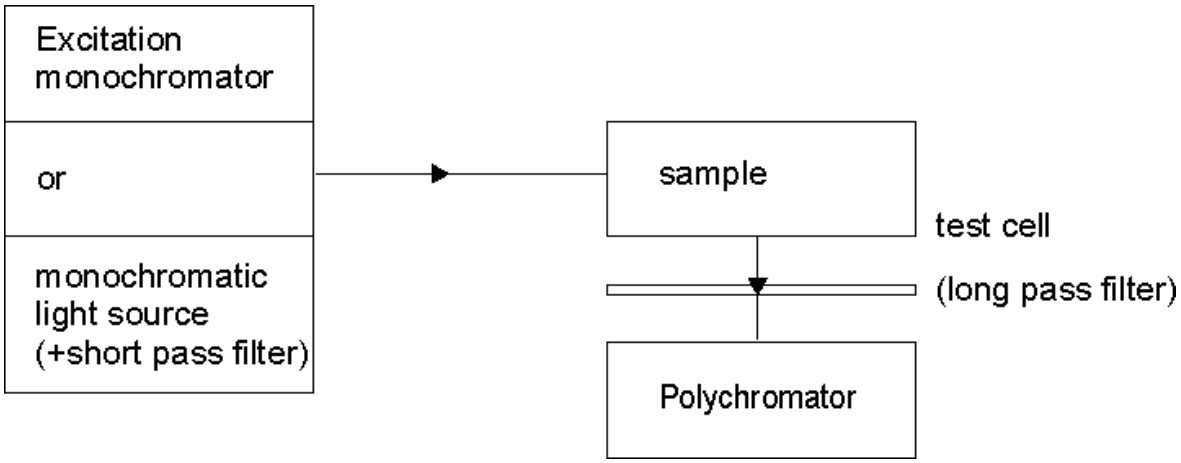


Fig. 20 Fluorescence measuring set-up

The differentiation of the reflected/ transmitted and the fluorescence signal is only possible by a spectral separation on excitation **and** emission side. This measuring set-up is called bispectral. Laboratory set-ups consist of two monochromators, which both are tuned. Such arrangements have a high sensitivity, but a long measuring time. The result is a three dimensional spectrum (reflexion/ transmission and fluorescence over the wavelength).
The measuring geometries of reflexion set-ups are equal to those in pure reflexion spectroscopy (see fig. 23). In case of illumination by a sphere the emitted fluorescence light acts as a secondary source for the probe. Furthermore, glance effects have to be taken into account. In 45°/ 0° set-ups these effects do not matter.
The measurement of liquids or dissolved materials is commonly done in special test cells, suited for fluorescence measurement. The illumination angle is 0°, the fluorescence signal is measured under an angle of 90° to the illuminant to reduce the influence of the excitation energy (see fig. 30).

In fluorescence measurement it is necessary to pay attention to several main points:

- The absorption band of the sample has to be known or has to be measured (to know the wavelength for most effective excitation).
- The fluorescence intensity is relatively low, therefore it is necessary to suppress the influence of the excitation energy on the measuring signal (filters, geometry).
- The quantum yield of materials is very different, e.g. Rhodamine B has a very high yield, Eosin and Chlorophyll a substantial lower one.
- Fluorescence analysis is 100 ... 1000 x more sensitive than absorption spectroscopy. There can be analyzed mixtures with only one fluorescent part or media with different fluorescent components.
- The fluorescence intensity can be strongly temperature dependent. Furthermore, it can be quenched, especially by dissolved oxygen.
- The broadband excitation light can cause photochemical reactions, which can influence the fluorescence intensity,
- Impurities of the sample, of the solvent or the test cell can influence the fluorescence signal.
- Stray light (Rayleigh) can cause additional peaks, which have to be distinguished from the fluorescence signal.

The following figure shows an examplary fluorescence spectrum, obtained by the reflexion measurement of a fluorescence marker in a bank note. Furthermore, the excitation spectrum (UV LED) as well as the transmission spectra of two blocking filters are shown.

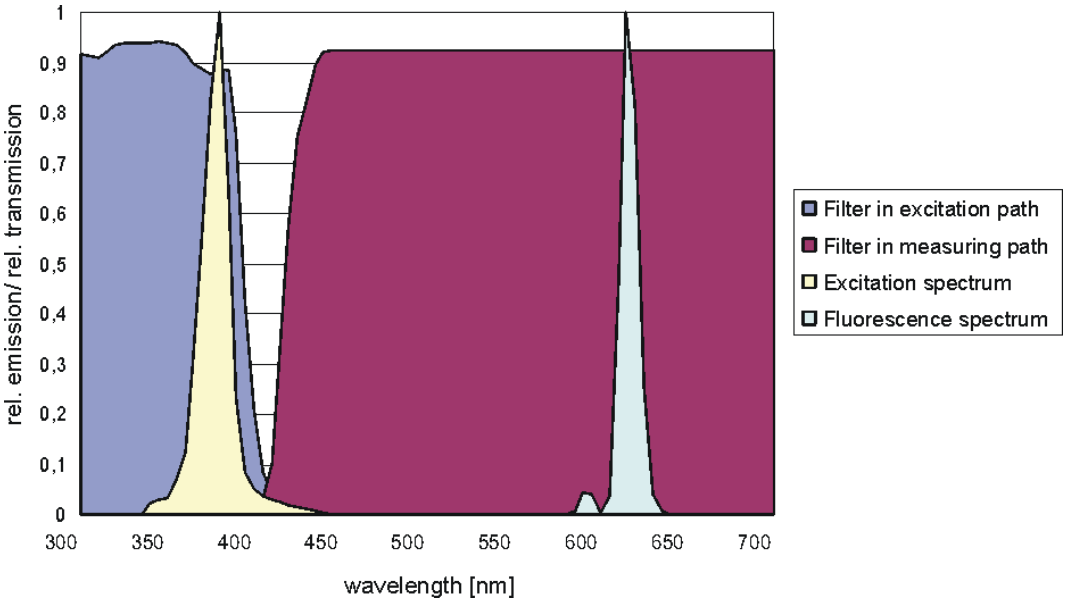


Fig. 19 Fluorescence spectrum example (Fluorescence marker of a bank note)

From this short survey can be seen that line array spectrometers show several advantages in fluorescence measuring applications especially for economic set-ups for production control.

3.6 Multichannel Spectral Measurement

The simplest multichannel measurement has been used for many years – the referencing of a light source with a second spectrometer. During the last 10 years applications with more channels have become more and more of interest.
First, there is to clarify one misunderstanding: Some publications define the detection of one spectrum as multichannel detection due to the parallel read out of the pixel of the line array – which contains much more information than available from a filter instrument. Multichannel in the sense here means the read out of at least two separate measuring spectra. Application examples are quality control of light sources during fabrication process, color measurement and pharmaceutical high throughput measuring instrumentation.
This read out of the spectra can be done in two ways – serial or parallel. Both kinds show specific advantages and disadvantages.

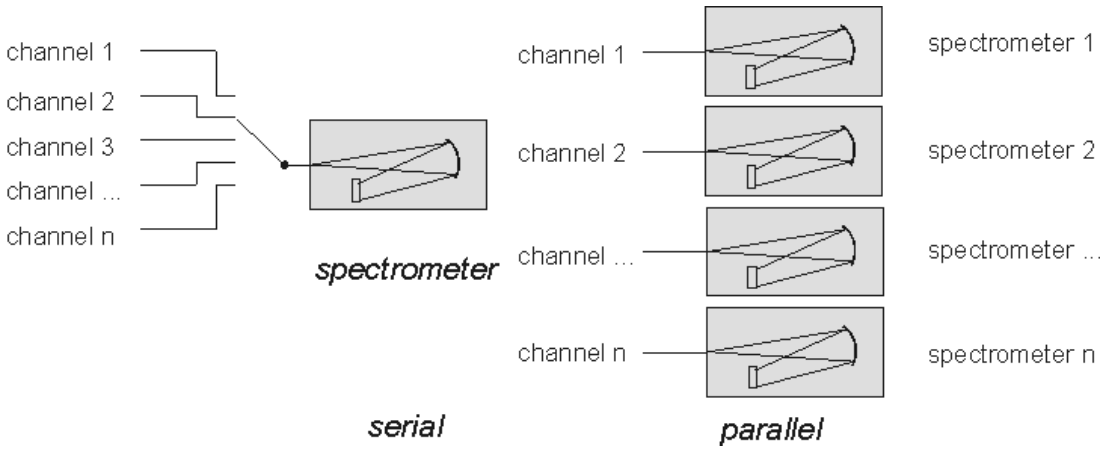


Fig. 20 Serial and parallel multichannel spectral measurement

	Serial read out	**Parallel read out**
Set-up	Optical switch (mainly fiber switch) + one spectrometer	One spectrometer per channel
Measuring time	long (Channel number * measuring time per channel)	Short (only one integration + read out time)
Calibration/ referencing	only one spectrometer	Each spectrometer separately
Reproducibility	Reproducibility of switch is included in the measuring result	No mechanical movement – higher reproducibility
	Changes of measuring object are possible during sequential channel read out	Same conditions for all channels during read out
Cost	Considerable costs of optical switch	Costs for several spectrometers
Applications	Mainly where high end spectrometers are needed	Fast measuring applications

The JETI product is based on a simultaneous (parallel) measurement with a separate spectrometer per channel. The costs of miniaturized spectrometers decreased during the last years, so this solution becomes more and more of interest. The following figure shows a 9 channel spectroradiometer MCR-09 with the software displaying all spectra simultaneously This instrument contains a fiber shutter for an easy dark correction.

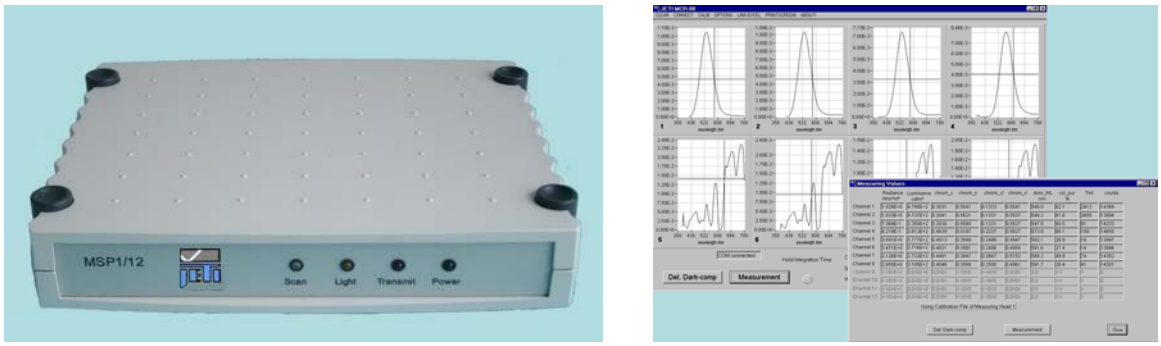


Fig. 21 6 channel spectrometer and screen shot of the PC software

Examples for applications of this technical solution are:

- Spectral measurement of multi LED equipped PCB´s
- Long term observation of lamp burn in tests
- Multi angle color measurement

Typical parameters for spectrometric multichannel systems are:

• Channel number	2 ... 12
• Intergration time	10 ms ..... 1 s
• Read out time	4 ... 20 ms
• Repetition rate	up to 10 Hz

The read out of the JETI multichannel instruments is proceeded pixelwise. The single pixel signals from all channels are fitted into each other. So it is guaranteed that no jitter appears between the spectra.

Table of Figures