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PHOTONIC MICRO SENSORS FOR MOBILE COLOR AND SPECTRAL CHARACTERIZATION OF COLORED LIQUIDS IN LABORATORIES AND IN FIELD

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Abstract – Aim of the paper is to show that the colorimetric characterization of optically clear colored liquids can be performed with so called dielectric-interference multi-spectral micro sensors in comparison to spectral sensors. Multi-spectral micro sensors and spectral sensors are differentiated by their spectral resolution, measurement speed, accuracy and cost. Multi-spectral micro sensors are less expensive. The paper describes how dielectric-interference multi-spectral micro sensors are calibrated with application specific calibration methods and conventional liquid color standards, methodically and theoretically. The paper proofs that and how dielectric-interference multi-spectral micro sensors can be applied with smartpads for the calculation of measurement results both in laboratory and in field. A given practical example is the application for the colorimetric characterization of petroleum oils and fuels and their colorimetric characterization by the Saybolt color scale.

Keywords: multi-spectral micro sensors, photonic micro sensors, color, spectral

1. SUBJECTIVE LIQUID COLOR INSPECTIONS

In chemical, pharmaceutical and cosmetic industries the quality demands for colored liquids are growing. Typical colored liquids are solvents, oils, fatty acids and fuels. The quality of optically clear liquids is characterized for example by their colors. For different liquids a bigger number of characterizing standards and scales in the past have been developed and applied (Fig. 01) [01].

Colored Liquids	Liquid and Application Specific Color Characterization
Chemicals & industrial oils	Pt-Co/Hazen/APHA, Garner, Iodine, CIE values, spectral data
Petroleum oils & fuels	Saybolt, ASTM Color, Pt-Co/Hazen/APHA, CIE values, spectral data
Dark oils & fats	FAC, Gardner, CIE values, spectral data
Beers, malts and caramel	EBC (CIE & 430 nm), ASBC (CIE & 430 nm), CIE values, spectral data
Pharmaceutical solutions	EUR, US & Chinese Pharmacopoeia Color, Pt-Co/Hazen/APHA, CIE values, spectral data
Industrial oils and surfactants	Klett Color (blue filter KS-42), Pt-Co/Hazen/APHA, CIE values, spectral data
Sugars, syrups and honeys	ICUMSA Color (420, 560, 710 nm), Honey Color, CIE values, spectral data
Water & wastewater	ADMI (spectral & tristimulus filter methods), Pt-Co/Hazen/APHA, CIE values, spectral data
Transparent liquids	CIE values, L*a*b* or L*C*h* color space, Hunter Lab color space, spectral data

Fig. 01. Liquid specific colorimetric characteristics

Nowadays the color analysis of liquids can be applied by the so called:

- subjective visual color inspection method, where qualified inspection persons compare **subjective** the investigated liquid probes with defined mechanical color standards or
- objective tristimulus, multi-spectral and spectral measurement methods where measurement systems compare **objective** the investigated liquid probes with defined electrical color standards

A fundamental preposition for objective quality assurance are appropriate measurement systems. Innovative measurement systems are combinations of photonic micro sensor modules and digital image processing with smartpads. These systems are **mobile** applicable in laboratories and in field (Fig. 02) [02] [03] [04] [05] [06] [07].

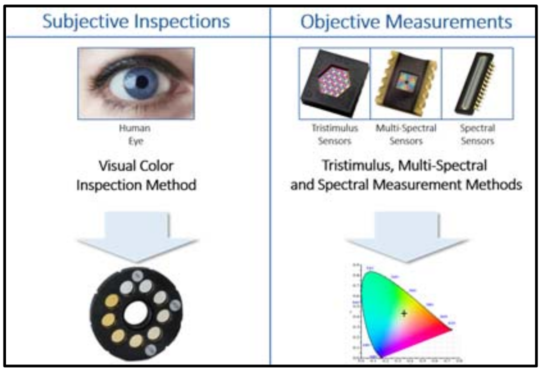

Fig. 02. From subjective inspections to objective measurements

In the International Vocabulary of Metrology calibration is defined (VIM 2.39): “**Calibration** is an operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication.”

Calibration standards for color inspections and measurements are manifold (Fig. 03) [08] [09] [10] [11] [12].

Calibration LEDs (Emission)	X-Rite Color Checker (Reflection)	RAL Color Fan (Reflection)	Lovibond Color Liquids (Transmission)	Lovibond Color Glasses (Transmission)

Fig. 03. Calibration standards for color inspections and measurements

Calibration standards can be used to match the capabilities, performance and ease-of-use of smart mobile photonic micro measurement systems. Concerning the differences between laboratory and in-field measurements the environmental conditions for in-field measurements might be more complex than in laboratory. Nevertheless the resolutions, accuracies and reproducibilities of laboratory and in-field measurements should be more or less equal. Main problem is the task specific calibration of in-field measurement systems. The colorimetric characterization of optically clear colored liquids with calibrated multi-spectral micro sensor modules is documented in the DIN EN 1557, 1997 [13] and the ASTM E 308 – 99, 2013 [14]. The determination for example of Saybolt color numbers is documented in ASTM D 6045 – 96, 2013 [15]. Aim of the investigations was the color and spectral characterization of optically clear colored liquids which can be described by the Saybolt color scale. The Saybolt color scale is an empirical scale from −15 (darkest) to +30 (lightest) to express the colors of clear petroleum oils and fuels (Fig. 04) [15].

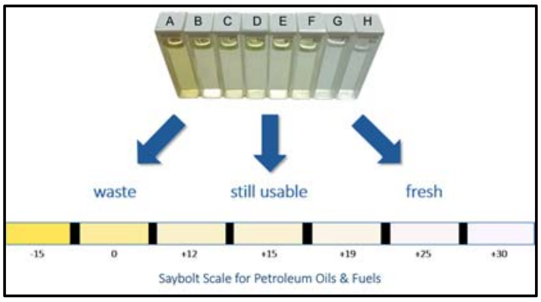

Fig. 04. Liquid probes (top), quality of liquid probes (center) and Saybolt color scale for liquids (down)

The Saybolt color scale is used not only for the colorimetric characterization of petroleum oils and fuels but also for a wide variety of petroleum products such as undyed motor and aviation gasoline, aviation turbine fuels, naphthas, kerosine, pharmaceutical white oils, diesel fuel oils, heating oils, and lubricating oils [15].

3. OBJECTIVE LIQUID COLOR AND SPECTRAL MEASUREMENTS

The paper tackles also technologies for so called multi- and hyper-spectral micro sensors which can be used for objective measurements in industry, biology/medicine, agriculture/ environment, administration and security. Four different multi- and hyper-spectral micro sensor technologies can be distinguished.

3.1. Spectral Sensors

Spectral Sensors with digital image processing show the intensity of light as a function of wavelength. The deflection is produced either by refraction with prism or by diffraction with a diffraction grating (Fig. 05) [06].

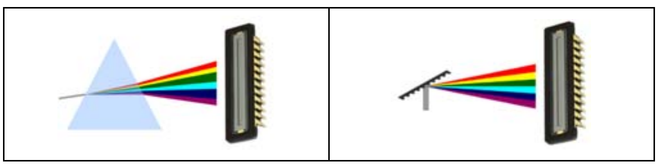

Fig. 05. Spectral sensor with prism (left) and grating (right)

3.2. Micro-Patterned Multi-Spectral Micro Sensors

Micro-patterned multi-spectral micro sensors have narrowband optical filters integrated on photodiodes. The patterning is a combination of dielectric, metal and conductive coatings. The micro-patterned technology enables specific spectral selective micro sensor design. An example setup was realized with 8 spectral channels into a 9.0 mm square footprint (Fig. 06) [16].

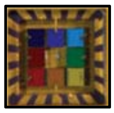

Fig. 06. Micro-patterned multi-spectral micro sensor

The photodiodes are configured for common cathode operation, providing low noise and fast temporal response. Targeted spectral bands can be in VIS and NIR bands from 400 nm up to 1000 nm.

3.3. Nano-Structured Multi-Spectral Micro Sensors

Nano-structured multi-spectral micro sensors have hole arrays as the spectral selective elements integrated on photodiodes. The used physical effect is called surface plasmon effect [17]. The nano-structured technology enables specific spectral selective sensor design. An example setup was realized with 16 spectral channels into a 2.5 mm square footprint (Fig. 07) [18].

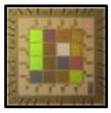

Fig. 07. Nano-structured multi-spectral micro sensor

The integration of amplifiers and signal processing is possible within CMOS-processes. Targeted spectral bands can be in VIS and NIR bands from 400 nm up to 1000 nm.

3.4. Dielectric-Interference Multi-Spectral Micro Sensors

Dielectric-interference multi-spectral micro sensors have titanium dioxide and silicon dioxide filter stacks as the spectral selective elements integrated on photodiodes. The dielectric-interference technology enables specific spectral selective sensor design. An example setup was realized with 6 spectral channels into a 2.4 mm square footprint and all in all in a SMD chip with 7.0 x 6.0 x 1.7 mm (Fig. 08) [19].

Fig. 08. Dielectric-interference multi-spectral micro sensor

The dielectric-interference filters show no aging in comparison to absorption filters and have no thermal drifts. Targeted spectral bands can be in VIS and NIR bands from 400 nm up to 1000 nm.

3.5. Fabry-Pérot Interferometric Hyper-Spectral Micro Sensors

Fabry-Pérot interferometric hyper-spectral micro sensors have Fabry-Pérot interferometric filter on top of each pixel as the spectral selective elements. Fabry-Pérot interferometric hyper-spectral technology enables a spatial spectral selective sensor design. Example setups were realized as so called line-scan, snapshot-tiled and mosaic into ceramic 95 pin PGA and uPGA 18.6 mm x 18.6 mm packages (Fig. 09) [20].

		
LINE-SCAN	SNAPSHOT-TILED	MOSAIC
• 100+ spectral bands • 600-1000 nm, 4 nm incremental steps • FWHM 10-15 nm • Spatial resolution 2048 x (100+ each band x 8 pixels)	• 32 spectral bands • 600-1000 nm, 12nm incremental steps • FWHM 10 - 15 nm • Spatial resolution per band: 256 x 256	• 4x4 mosaic, 16 spectral bands • 470-630 nm, 11 nm incremental steps • FWHM 10 - 15 nm • Spatial resolution per band: 512 x 272, up to 2 mpix with interpolation

Fig. 09. Fabry-Pérot interferometric hyper-spectral micro sensors

The hyper-spectral filters are integrated monolithically on top of the sensor at wafer-level. That provides high-level performance with significant reduction in size and cost. Targeted spectral bands can be in VIS and NIR bands from 470nm up to 1000 nm.

4. MULTI-SPECTRAL MICRO SENSOR MEASUREMENT VALUE INTERPRETATION

Nowadays the evaluation of colors can be accomplished by either colorimetric or radiometric values. That results in the usage of spectral information for the calculation of the tristimulus color values and their transformation into color spaces. The advantage is that a higher information density can be gathered for color measurement purposes. The resulting tristimulus values can be used for further transformations into any other color scales (see Fig. 01). The outputs of the investigated multi-spectral micro sensors are depending from the used illuminations and the investigated probes. For the transfer of the specific multi-spectral micro sensor outputs into standardized, for example Saybolt color numbers, a calibration must be accomplished [21]. A common calibration method is the application of a so called target based **correction matrix**. The correction matrix is based on a general comparison of existing reference values (or measured values of a spectral sensor) with the actual values of a multi-spectral micro sensor. The measurements of the values are realized by parallelization of a spectral sensor and a multi-spectral micro sensor. The relationship between the **spectral sensor values** ($\underline{T}$) and the **multi-spectral micro sensor values** ($\underline{S}$) are used for the target based correction matrix (1).

$$\underline{T} = \underline{K} \cdot \underline{S} \qquad (01)$$

After transposition of equation (01) into the correction matrix $\underline{K}$ (02) the corrected measurement values can be calculated by:

$$\underline{K} = \left(\underline{T} \cdot \underline{S}^T\right) \cdot \left(\underline{S} \cdot \underline{S}^T\right)^{-1} \qquad (02)$$

For a compensated, balanced and calibrated multi-spectral micro sensors the following steps have to be accomplished:
Calibration Step 1- Offset compensation: To eliminate potential errors by added electronic components the sensor must be darkened and a zero measurement must be performed. The amplification levels for color and dark measurements must be identical. The offset must be subtracted from the measurement signals of the multi-spectral micro sensor to enable the calculation of the correction matrix (02).
Calibration Step 2 - White balancing: White balance temperature and aging related spectral shifts of the optical system (multi-spectral micro sensor, illumination and optics) will be compensated by the following method: Comparison of the working multi-spectral micro sensor with an aging resistant white standard. For transmission measurements the white balancing is performed by the use of incident light as a reference.
Calibration Step 3 - Measurement with calibration standards: Comparison of the multi-spectral micro sensor and the spectral sensor as reference alternating with the linear independent calibration standards.
Calibration Step 4 - Calculation of the correction matrix: Calculation and application of the target based correction matrix for the measurement task. After the offset compensation, white balancing and calibrated measurements the multi-spectral micro sensors can achieve similarly accurate readings in the same color measurement applications as spectral sensors.

Further calibration methods for multi-spectral micro spectral sensors are: Eigenvalue method, Hardeberg method and Wiener method.

5. PRACTICAL EXAMPLE FOR QUALITY CONTROL OF COLORED LIQUIDS

The practical example deals with the application of dielectric-interference multi-spectral micro sensors for the colorimetric characterization of petroleum oils and fuels and furthermore their colorimetric characterization by the Saybolt color scale. To verify the measurement results the color difference ΔE has been determined between multi-spectral micro sensor and spectral sensor measurement values (Tab. 01 and Fig. 10) [22].

Tab. 01. Color difference ΔE between the calibrated multi-spectral micro sensor and the spectral sensor (red - outside Saybolt scale)

	A	B	C	D	E	F	G	H
ΔE	0,047	0,036	0,072	0,151	0,068	0,098	0,066	0,185

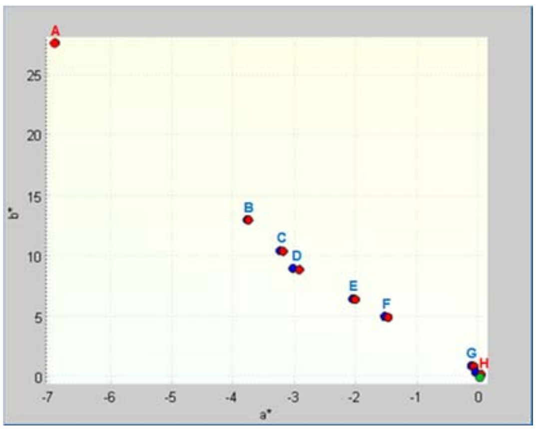

Fig. 10. Color difference ΔE between the calibrated multi-spectral micro sensor and the spectral sensor - **Color Values:** Normal Probe | Multi-Spectral Micro Sensor | Spectral Sensor

The determined color differences are relatively small and in line with expectations. As a result of the target based calibration the color differences ΔE between multi-spectral micro sensor and spectral sensor for the specified measuring samples have a color difference of $\Delta E < 1$. The use of liquid Saybolt calibration standards for the target based calibration of multi-spectral micro sensors proves to be promising for practical applications. With the color differences of Saybolt calibration standards to the normal probe a Saybolt calibration curve is generated using a logarithmic trend line. The Saybolt color values of the measured probes are determined by the equation (y) of the calibration curve (Fig. 11) [22].

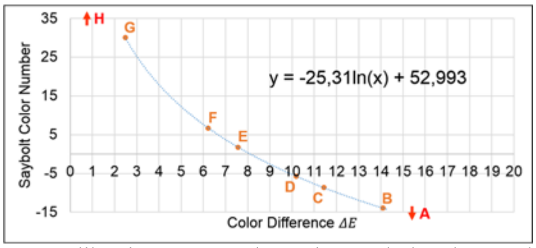

Fig. 11. Calibration curve to determine Saybolt color numbers

As a result, the determination of Saybolt color numbers is in very good coincidence with the reference values of the spectral sensor. The calculation of Saybolt color numbers has shown that the test probes can be distinguished on the Saybolt color scale. As a result, the determination of the Saybolt color numbers of the test probes B, C, D, E, F and G are possible (Tab. 02) [22].

Tab. 02. Measurement results for test probes in Saybolt color numbers

	A	B	C	D	E	F	G	H
Multi-Spectral Micro Sensor	-32,27	-14,02	-8,78	-6,05	1,57	6,40	29,83	42,24
Spectral Sensor	-32,31	-13,96	-8,65	-5,75	1,74	6,71	30,05	42,98
Saybolt Scale	-15 0 +12 +15 +19 +25 +30							

6. SUMMARY AND CONCLUSIONS

Aim of the paper was a theoretical and experimental comparison of the colorimetric characterization of optically transparent liquids with multi-spectral micro sensors and spectral sensors. Subject matter of the investigations have been petroleum oils and fuels, which can be described as a result of the colorimetric characterization on the Saybolt color scale. It was clearly demonstrated that the quality of petroleum oils and fuels can be tested with mechanical standards and measured either with multi-spectral micro sensors or spectral sensors. Therefore the usual subjective color tests can be replaced for petroleum oils and fuels by mobile objective color measurements. In the present paper it has been shown evidently that objectified mobile color measurements of petroleum oils and fuels can be realized by multi-spectral micro sensors and smartpads in a convenient, reliable and affordable way. Further on it has been proved, that multi-spectral micro sensors with smartpads are capable for the generalization of mobile measurements of optically transparent liquids. That means:

- Innovative convenient, reliable and affordable measuring instruments with photonic micro sensor modules, smartpads and software apps enable objective colorimetric characterizations of optically transparent liquids at the point of interest.
- Multi-spectral micro sensor modules have the same color accuracy as spectral sensor modules in terms of colorimetric characterizations for optically clear colored liquids.
- Highly accurate colorimetric characterizations of liquids according to DIN EN 1557 and ASTM D 6045 - 96 can be seamlessly applied to calibrated multi-spectral micro sensor modules.
- Image processing software apps can be unified for the numerical and graphical representation of color spectra and color coordinates in the color spaces.

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REFERENCES

[01] Lovibond - The Tintometer Ltd., „Lovibond® PFXi-195 Series - Accurate, efficient spectrophotometric colorimeters“, Amesbury, UK, 2010

[02] www.imgarcade.com, “Gallery For > Human Eye”, [Online], Available: http://imgarcade.com/1/human-eye/. [Zugriff am 15 Februar 2014].

[03] Orbeco-Hellige Inc., “Color | Orbeco-Hellige - Laboratory and Field Instruments and Reagents for Water Analysis and Color Measurement”, [Online], Available: http://www.orbeco.com/color. [Zugriff am 15 Februar 2014].

[04] MAZeT GmbH, „Datenblatt: MTCSiCF Integral True Color Sensor – QFN16“, Jena, 14.02.2014.

[05] MAZeT GmbH, „Datenblatt: MMCS6CS 6-channel Multiple Color Sensor – LCC10“, Jena, 07.01.2014.

[06] Hamamatsu Photonics K.K., “Back-thinned type CCD linear image sensor S11155-2048-01 | Hamamatsu Photonics”, [Online], Available: http://www.hamamatsu.com/jp/en/product/alpha/C/4206/4214/S11155-2048-01/index.html. [Zugriff am 15 Februar 2014].

[07] Wikipedia, “International Commission on Illumination - Wikipedia, the free encyclopedia”, [Online], Available: http://en.wikipedia.org/wiki/International_Commission_on_Illumination. [Zugriff am 15 Februar 2014].

[08] Instrument Systems GmbH, "ACS LED-Kalibriernormale - Instrument Systems", [Online], Available: http://www.instrumentsystems.de/produkte/led-messzubehoer/acs-led-kalibriernormale/. [Zugriff am 15 Februar 2014].

[09] X-Rite Inc., "X-Rite: MSCCC: ColorChecker Classic", [Online], Available: http://xritephoto.com/ph_product_overview.aspx?id=1192. [Zugriff am 15 Februar 2014].

[10] Wikipedia, "RAL-Farbe – Wikipedia", [Online], Available: http://de.wikipedia.org/wiki/RAL-Farbe. [Zugriff am 15 Februar 2014].

[11] The Tintometer Ltd, "Liquid Standards- Lovibond Colour", [Online], Available: http://www.lovibondcolour.com/liquid-standards. [Zugriff am 15 Februar 2014].

[12] The Tintometer Ltd, "Glass Standards- Lovibond Colour", [Online], Available: http://www.lovibondcolour.com/glass-standards. [Zugriff am 15 Februar 2014].

[13] DIN - Deutsches Institut für Normung e.V., „DIN EN 1557 - Colorimetric characterization of optically clear colored liquids (products) as X, Y, Z tristimulus values in transmission“, Beuth Verlag GmbH, Berlin, 1997.

[14] ASTM International, „ASTM E 308 - 99 - Standard practice for computing the colors of objects by using CIE system“, ASTM International, ASTM D 6045 - 96, 2013.

[15] ASTM International, „ASTM D 6045 - 96 - Standard test method for color of petroleum products by the automatic tristimulus method“, ASTM International, West Conshohocken, 2013.

[16] PIXELTEQ, "Multispectral Imaging & Sensing Solutions for the UV to SWIR", Eric Chandler, [Online]. Available: http://spectronet.de/de/suche/multispectral-imaging-sensing-solutions-for-the-uv_hxf5m3sn.html. [Zugriff am 15 Februar 2014].

[17] T.W. Ebbesen, Extraordinary optical transmission through sub-wavelength hole arrays, Macmilian Publishers Ltd, 1998

[18] Fraunhofer IOSB, "Video: Optische Stoffcharakterisierung von Flüssigkeiten", Stephan Junger, [Online], Available: http://spectronet.de/de/suche/video-optische-stoffcharakterisierung-von-fl%C3%BCssigk_huv7aelt.html. [Zugriff am 15 Februar 2014].

[19] MAZeT GmbH, "Multiple Color Sensors - English", MAZeT GmbH, [Online], Available: http://www.mazet.de/en/products/jencolor/multiple-color-sensors?set_language=en. [Zugriff am 15 Februar 2014].

[20] Ximea GmbH, “Video: Miniature Hyperspectral Imaging Cameras”, Max Larin, [Online], Available: http://spectronet.de/de/videos_2014/video-miniature-hyperspectral-imaging-cameras_i3tabv8f.html. [Zugriff am 15 Februar 2014].

[21] K.-H. Franke und R. Nestler, Tagungsband der Beiträge zum 12. Workshop Farbbildverarbeitung, Ilmenau: ZBS e.V., 2006.

[22] Dittrich, Masterthesis, „Untersuchungen zur farbmetrischen Charakterisierung von optisch transparenten Flüssigkeiten mit mehrkanaligen Spektralsensoren“, Ernst-Abbe-Hochschule Jena, 2014.