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 possible applications for color inspections and measurements of liquids. The paper tackles different technologies of multi-spectral and spectral micro sensors which can be used in laboratories and in field - convenient, reliable and affordable. Multi-spectral and spectral micro sensors are differentiated by their spectral resolutions, measurement speeds, accuracies and costs. Multi-spectral micro sensors are less expensive. The paper describes how dielectric-interference multi-spectral micro sensors are calibrated. Practical applications for the colorimetric characterization of petroleum oils and fuels and their colorimetric characterization by liquid color scales are tackled.*

Keywords: Multi-Spectral Micro Sensors, Photonic Micro Sensors, Color, Spectral

1. Subjective Liquid Color Inspections

In chemical, pharmaceutical and cosmetic industries the quality expectations for colored liquids are growing. Typical colored liquids are solvents, oils, fatty acids and fuels. The qualities of optically clear liquids are 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 so called:
- subjective visual color inspection methods, 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].

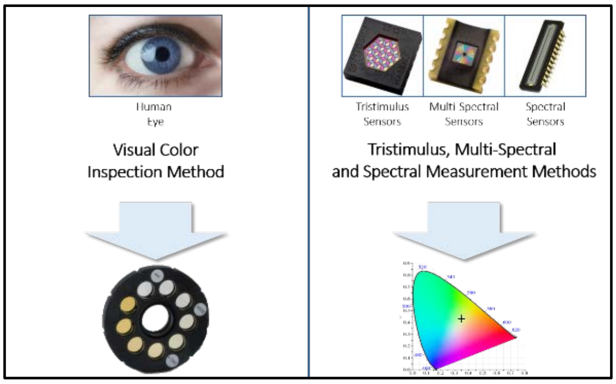

Fig. 02. From subjective inspections to objective measurements

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. 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 [04] and the ASTM E 308 – 99, 2013 [05]. The determination for example of Saybolt color numbers is documented in ASTM D 6045 – 96, 2013 [06]. 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. 03) [06].

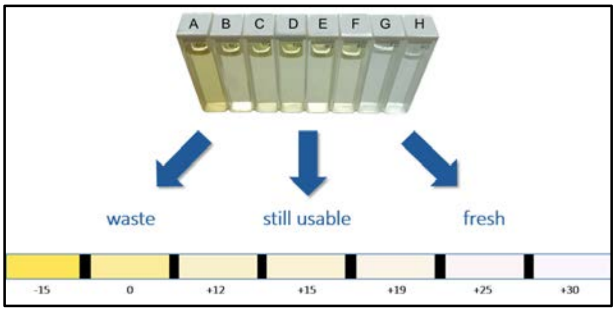

Fig. 03. Liquid probes (top), quality of liquid probes (center) and Saybolt color scale for liquids (down)

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, naphtha, kerosine, pharmaceutical white oils, diesel fuel oils, heating oils, and lubricating oils [06].

2. Objective Color and Spectral Measurements of Liquids

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. **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. 04) [03].

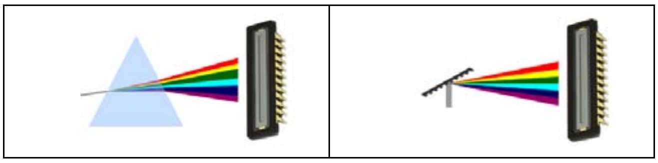

Fig. 04. Spectral sensor with prism (left) and grating (right)

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 a specific spectral selective sensor design. An example setup was realized with 8 spectral channels into a 9.0 mm square footprint (Fig. 05) [07]. The photodiodes are configured for common cathode operation, providing low noise and fast temporal response. Targeted spectral bands are located in VIS and NIR bands from 400 nm up to 1000 nm. **Nano-structured multi-spectral micro sensors** have sub-wavelength hole arrays as the spectral selective elements integrated on photodiodes. The used physical effect is called surface plasmon effect [08]. The nano-structured technology enables a specific spectral selective sensor design. An example setup was realized with 16 spectral channels into a 2.5 mm square footprint (Fig. 06) [09]. The integration of amplifiers and signal processors is possible within CMOS-processes. Targeted spectral bands are located in VIS and NIR bands from 400 nm up to 1000 nm. **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 a 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. 07) [10]. The dielectric-interference filters show no aging in comparison to absorption filters and have no thermal drifts. Targeted spectral bands are located in VIS and NIR bands from 400 nm up to 1000 nm.

Fig. 05. Micro-patterned multi-spectral micro sensor

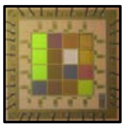

Fig. 06. Nano-structured multi-spectral micro sensor

Fig. 07. Dielectric-interference multi-spectral micro sensor

Fabry-Pérot interferometric hyper-spectral micro sensors have Fabry-Pérot interferometric filters 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 µPGA 18.6 mm x 18.6 mm packages (Fig. 08) [11].

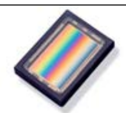		
LINE-SCAN	SNAPSHOT-TILED	MOSAIC
• 100+ spectral bands • 600-1000 nm, 4 nm incremental steps • FWHM 10-15 nm • Spatial resolution 2048 x (100+ each band x 8 pixels)	• 32 spectral bands • 600-1000 nm, 12nm incremental steps • FWHM 10 - 15 nm • Spatial resolution per band: 256 x 256	• 4x4 mosaic, 16 spectral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

Fig. 08. 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.

3. Multi-Spectral Micro Sensor Value Interpretation

For the transfer of the specific multi-spectral micro sensor outputs into standardized, for example Saybolt color numbers, a calibration must be accomplished [12]. 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 and a multi-spectral micro sensor. The relationship between the **spectral micro sensor values** ($\underline{T}$) and the **multi-spectral micro sensor values** ($\underline{S}$) are used for the target based correction matrix (01).

$$\underline{T} = \underline{K} \cdot \underline{S} \tag{01}$$

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

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

After a successful calibration colorimetric calculations according to standards can be applied. It is necessary to transfer the sensor outputs to the liquid specific color scales.

4. Summary and Conclusions

Aim of the paper was to show possible applications for color inspections and measurements of liquids with multi-spectral and spectral micro sensors. Different sensor technologies have been tackled. Subject matter of the investigations where optically transparent liquids like petroleum oils and fuels, which can be described as a result of the colorimetric characterization on the Saybolt color scale. In the presentation it will be shown that objectified mobile color measurements of petroleum oils and fuels can be realized by multi-spectral micro sensor modules in laboratories and in field.

Acknowledgements

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