Palm Oil – UV/Vis Spectrophotometric Quality Assessment Along the Value Chain Using the Deterioration of Bleachability Index (DOBI) and Carotene Content According to ISO 17932:2011

Challenge

Rapid and precise quality assessment of palm oil, and other edible oils, according to industry standards such as ISO 17932:2011.

Solution

The UV/Vis spectrophotometer SPECORD PLUS series allows fast and reliable evaluation of DOBI and carotene content in a wide range of samples including palm oil.

Introduction

Palm oil is one of the most relevant soft commodities and a key edible oil with a wide range of applications, reaching from plant-based cooking oil or fat, up to essential ingredient in convenience food, as well as biodiesel precursor. As an industry-essential raw material, palm oil is a high-yield agricultural product extracted from the fruit flesh (mesocarp) of oil palm trees (*Elaeis guineensis*). Originally from Africa, these are mainly grown in far east countries, predominantly in Malaysia and Indonesia. Upon harvest, the fresh fruit bunches are processed in mills at origin into crude palm oil (CPO). As by-products kernel and fuel are obtained in the milling process. CPO is subsequently shipped and stored in bulk prior to bleaching and refinement. Further downstream processing and incorporation into food and materials production follows.

To meet industry standards along the value chain, specific parameters at defined quality gates enable stakeholders to monitor raw material quality indicators, as well as track changes during the subsequent processing steps. In a high-throughput and high-volume industry rapid and reliable analytical methods which leverage reliable quality parameters are needed. Since initial palm oil quality parameters determine subsequent processing conditions as well as quality ranges, the assessment of CPO is of particular importance. Herein UV/Vis spectrophotometry has been proven as a powerful qualitative and

quantitative analytical tool since it allows the determination of various parameters, which are now incorporated into industry standards. Among them the "Determination of the deterioration of bleachability index (DOBI) and carotene content (ISO 17932:2011)"[1] is a paramount quality indicator for CPO and bleached palm oil. In addition, the systematic analysis of the UV/Vis spectra of palm oil at a different processing stages up to refined oils allows to survey the quality gates along the value chain.

In addition to the in triglycerides esterified fatty acids, crude palm oil is rich in carotenes (or xanthophylls), which provide the red-orange color to the CPO. These polyisoprene-derivates serve as radical scavengers in plants and are heavily sensitive towards oxidation and therefore they are good indicators of palm oil deterioration. Thus, and in agreement with the ISO 17932:2011, simply the ratio between the carotene absorption at 446 nm and the corresponding value at 269 nm, is an accepted indicator for the accumualtion of secondary oxidation products.[1] In this application note, the ScanDrop² and the SPECORD 50 PLUS, respectively a small-foot print and a high-precision and multi-purpose device were deployed. Furthermore, the simple handling and easy sample preparation as well as the user-friendliness of the software for acquisition and processing of relevant spectra is highlighted. Finally, Analytik Jena leverages years of experience in molecular spectroscopy, which come in handy in the rapid and uncomplicated performance towards simpler and insightful chemical analysis.

Materials and Methods

Samples and reagents

Following the ISO 17932:2011 "Determination of the deterioration of bleachability index (DOBI) and carotene content", the absorption spectra of three distinct palm oil samples were measured in isooctane (2,2,4-trimethylpentane, GC-grade):

- Crude palm oil (CPO)
- Bleached palm oil
- Refined palm oil

Measurement

Prior to the analysis, all quartz (QS) cuvettes were rinsed with isooctane three times to remove any possible contamination. The here investigated palm oil samples solidified below 40 °C, thus all samples were heated in a water bath at 60 – 70 °C for 20 – 30 minutes until reaching a clear oil solution. If that is not the case, the oil sample can be filtered (filter paper Whatman No. 1). Approximately 0.1 g of the sample were weighed (0.001 g scale-precision) in a 25 mL volumetric flask (ISO 1042, class A), filled up with isooctane and homogenized. Eventually, 2.5 mL of the palm oil solution were filled into the cuvettes for each measurement. Prior every measurement, the cuvette was rinsed with the sample solution three times, thus removing any potential contamination.

Instrumentation and software settings

UV/Vis absorption was recorded either in a SPECORD 50 PLUS or in a ScanDrop² spectrophotometer. Both systems provide diverse advantages. While the

- SPECORD 50 PLUS double beam spectrophotometer is especially suited for highest spectroscopic performance and versatility towards high sample throughput, whereas
- the ScanDrop² equipped with a Xe-flash lamp leverages operation on a small bench footprint, no warm-up time and full spectrum acquisition (220 to 1000 nm) in less than 2 seconds.

For the purpose of the palm oil analysis, standard spectrophotometer parameters specified in the ASpect UV (SPECORD 50 PLUS) and the FlashSoftPro² (ScanDrop²) spectrometer software variants were followed. In both cases it required acquisition of the absorbance of the reference matrix, in this case isooctane, and subsequently the absorbance spectrum (ScanDrop²) or the absorption at 269 nm and 446 nm (SPECORD 50 PLUS) of each sample. In the latter case, the absorbance at the selected wavelength was recorded in the photometry module with an integration time of 0.1 s. The recorded spectra were first visually analyzed. Subsequently the DOBI and carotene content were calculated according to the ISO 17932:2011. Herein the DOBI-value (I_{DOB}, see Formula 1) was derived from ratio of absorbance at the 446 nm (A_{446}) and at 269nm (A_{269}).

$$I_{DOB} = \frac{A_{446}}{A_{269}} \quad (1) \qquad w_C = \frac{383\ \Delta A}{l\ \rho} \quad (2)$$

The carotene content (w_c, see Formula 2) was calculated by multiplying the pure carotene absorbance ΔA (at 446 nm without solvent contribution), the ratio of the percentage solution extinction coefficient of β-carotene in isooctane at 446 nm (value of 383) and the concentration ρ (in g/100 mL) of the palm oil/isooctane solution (Table 2) multiplied by the optical path length l (1 cm). The carotene concentration is then given in mg/kg. The ASpect UV software allows a built-in function to easily calculate the DOBI (Figure 1).

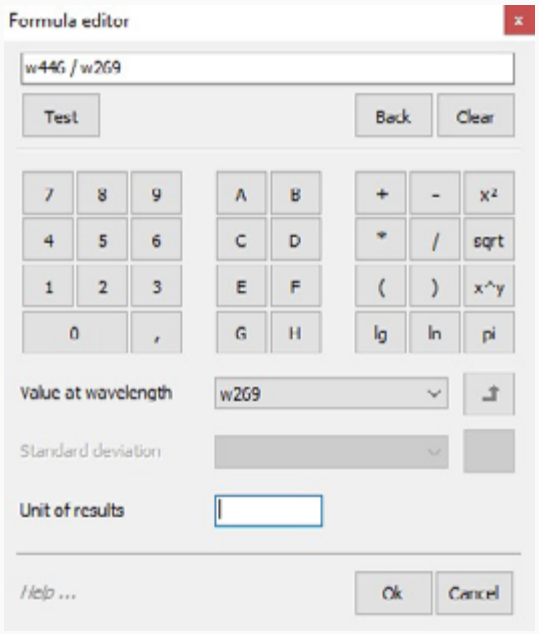

Figure 1: Formula editor of the ASpect UV software

Results and Discussion

In the first step the recorded spectra were analyzed. The absorption spectra of CPO (Figure 2), bleached and refined palm oil (Figure 3) are shown in the region from 250 up to 600 nm and can be largely assigned to carotene absorption. Here the highest absorption is recorded in the region of 400 – 500 nm. This feature in palm oil spectra contains solely contributions of pure carotenes, whereas features in the regions between 260 – 320 nm and 320 – 380 nm contain minor contributions of other compounds such as tocopherols. Most importantly, increase of secondary carotene degradation product formation can be easily monitored within the lowest UV-region (260 – 320 nm), especially at 269 nm. Precisely this feature is used in the ISO 17932:2011 to leverage the quality evaluation as the DOBI-value.

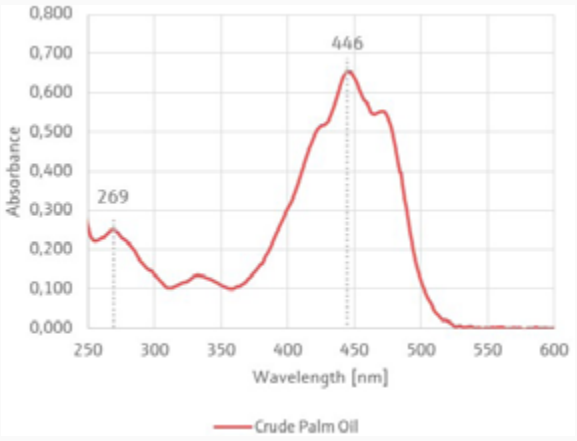

Figure 2: UV/Vis spectrum of CPO in isooctane

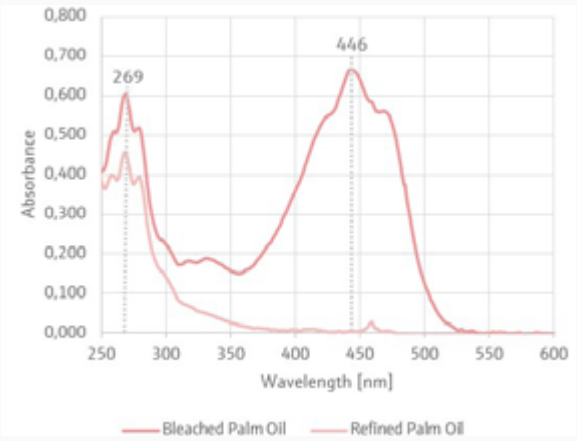

Figure 3: UV/Vis spectrum of bleached and refined palm oil in isooctane

Visual inspection of the spectra of the bleached and refined palm oil revealed key differences to the CPO spectrum, which are relevant for the quality assessment within the downstream value chain. Upon bleaching changes in color and thus partial degradation of carotenes led to a substantial increase of the absorption band with a maximum at 269 nm. For samples of the subsequent refinement process steps, the recorded absorption spectrum lacks any feature above approx. 400 nm, thus clearly indicating the absence of pure carotenes (Figure 3). However, the strongest feature with a maximum at 269 nm is clearly visible indicating that largely the secondary (carotenes) degradation products are present in reasonable amounts.

In the second step and following the procedures described in the ISO 17932:2011 the DOBI value(s) and carotene content(s) were calculated. Furthermore, the experimental results were validated with well-established oil quality standards correlated with estimated DOBI values.[1,3] In the current work, a DOBI value for CPO of 2.45 was estimated. According to Table 1, this corresponds to a fair quality CPO. Upon bleaching the DOBI value drops to 1.051, which is due to an intended degradation of carotenes and thus a corresponding enrichment of secondary degradation products exhibiting a higher absorption at 269 nm. Upon refinement the absorbance at 446 nm is (almost) zero, largely indicating the removal of carotenes and thus a substantial change in the color in comparison to CPO and bleached palm oil.

Table 1: Palm oil quality grading according to DOBI values[3]

DOBI	Palm oil grade
3.24	Excellent
2.93 – 3.24	Good
2.31 – 2.92	Fair
1.68 – 2.30	Poor
< 1.68	Sludge

Following the ISO 17932:2011 standard, the carotene content for all processing stages was estimated. Here an initial concentration of 553.0 mg/kg was determined. Upon bleaching the concentration dropped to 413.0 mg/kg and finally refinement led to a concentration of 21.0 mg/kg. Within this investigation, a performance comparison of the ScanDrop² and the SPECORD 50 PLUS devices for the determination of carotene concentration was conducted.

While carotene concentration for CPO and bleached palm oil (Table 2) differ by only 6 – 12 mg/kg or 2.1%, the higher performance and thus higher sensitivity of the double beam system in the SPECORD 50 PLUS spectrophotometer allowed a higher accuracy at the lower detection range and thus a more precise determination of the carotene content in the refined palm oil. Here, the carotene content in refined palm oil was found at 21.02 mg/kg (SPECORD 50 PLUS) and 3.24 mg/kg (ScanDrop²) respectively. To accelerate the measuring steps and still keep the DOBI determination accordingly to the norm, absorbance measurements solely at the given wavelengths (269 and 446 nm) might be performed. Here this is demonstrated with SPECORD 50 PLUS results (Table 2).

Table 2: Recorded absorption values, weighted amount of oil, estimated DOBI values as well as carotene content. Values in brackets correspond to measured absorbance or estimated values with the ScanDrop² spectrometer

Sample	A (269 nm)	A (446 nm)	DOBI	Conc. ρ in g/100 mL	Carotene in mg/kg
CPO	0.2605 (0.248)	0.6376 (0.651)	2.448 (2.625)	0.4416	553.0 (564.6)
Bleached	0.6190 (0.605)	0.6505 (0.661)	1.051 (1.092)	0.6032	413.0 (419.7)
Refined	0.5074 (0.458)	0.0324 (0.005)	0.064 (0.011)	0.5904	21.02 (3.24)

Conclusion

Analytik Jena leverages a long-term expertise in UV/Vis spectrophotometry, high-quality and endurable spectrophotometer systems such as the SPECORD 50 PLUS and hands-on solution in the determination of key quality parameters for plant-based edible oils. In the current study case, the quality of palm oil has been assessed along the value chain. According to the ISO 17932:2011, DOBI value(s) and carotene content were determined for crude palm oil (CPO), bleached as well as refined palm oil. Spectrophotometry-based quality assessment allows rapid and reliable evaluation without extensive sample preparation steps. In addition, the SPECORD 50 PLUS spectrophotometer has been successfully deployed for the analysis of palm oil quality at key steps of the value chain. In contrast to Xe-flash lamp systems (e. g. ScanDrop²), which are clearly designed for rapid detection, the SPECORD 50 PLUS and the corresponding ASpect UV software are well designed for accurate parameter evaluation, from high carotene concentrations in CPO, through the processing to bleached oil and downstream products like refined palm oil. Herein it is important to stress out the device's performance in the lowest detection range, allowing accurate low carotene content determination. Altogether the SPECORD 50 PLUS is a reliable tool for quality assessment along the palm oil value chain, providing unique hands-on expertise in edible oil analysis along the span of the value chain.

References

[1] DIN EN ISO 17932:2011-12

[2] Jolayemi, O. S.; Ajatta, M. A. and Adegeye A. A.; Geographical discrimination of palm oils (Elaeis guineensis) using quality characteristics and UV-visible spectroscopy; Food Sci Nutr. 2018, 6, pages 773–78

[3] Lin, S. W., DETERIORATION OF BLEACHABILITY INDEX, MPOB INFORMATION SERIES, 2004m MPON TT No.253, page 186

Headquarters
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0 · Author: FrEs, SaWu, MaHe
en · 02/2021