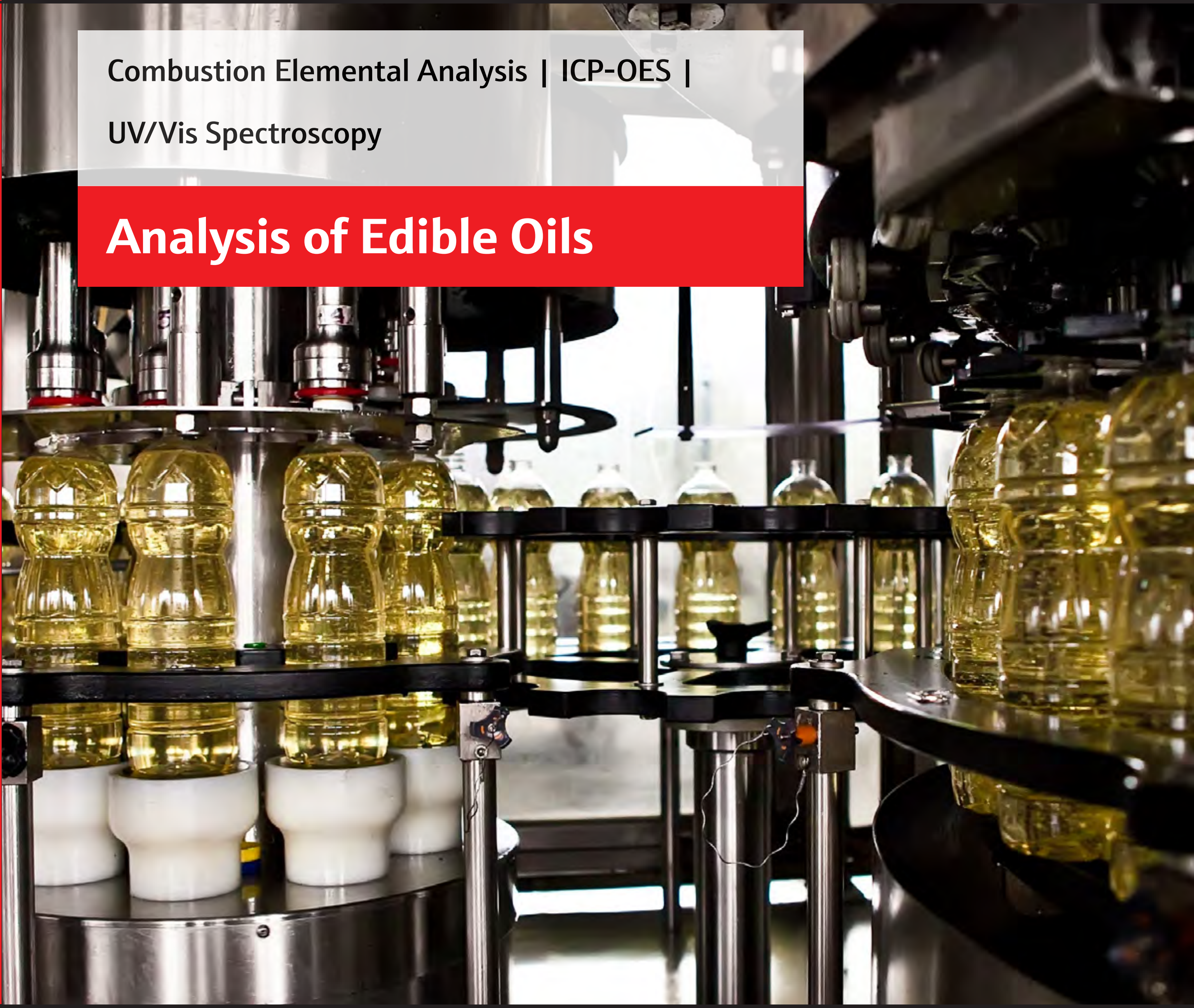
solutions



Combustion Elemental Analysis | ICP-OES |
UV/Vis Spectroscopy

Analysis of Edible Oils

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An Endress+Hauser Company

Dear readers,

Today, edible oils are everywhere. Oils like olive or sunflower are staples in many household cupboards and professional kitchens around the world. However, the global importance of edible oils lies mainly in their use as an ingredient in the production and processing of other food products, as well as cosmetics, and as a precursor for biofuels and oleochemicals. Vegetable oils are especially significant here: Today, the annual production of vegetable oils such as palm, palm kernel, rapeseed, soybean, coconut, peanut, and sunflower oil has gone up to over 200 million tons a year. They count as the most widely used oils with the highest annual production tonnage. Monitoring edible oil along the value chain for quality and safety parameters is a key task for food production companies and authorities – to protect consumers and to keep production values and standards high. Considering the complexity and the sheer amount of production taking place around the world, the challenge for laboratories is to cope with the increasing number of samples while simultaneously gain reliable analytical data.

Our company’s mission is to support customers worldwide with analytical solutions to improve their services and products. This e-book follows this intention. The methods and technologies presented support you in meeting the challenges of edible oil analysis more easily, reliably, and effectively. We discuss a series of quality parameters, food safety parameters as well as process efficiency indicators for edible oils. The e-book outlines the value chain of edible oil and indicates where the analysis of element contents as well as probing oil degradation at molecular level are meaningful and routinely performed. The e-book covers three core analytical techniques and topics: Combustion elemental analysis to efficiently monitor chlorine contents in palm oil, the assessment of trace element contents in edible oils utilizing ICP-OES (atomic spectrometry), and the assessment of the quality of materials and refines or intermediate products on a molecular level using UV/Vis spectroscopy.

We hope this e-book provides many valuable insights for you. If you have any questions about the methods and solutions presented, please do not hesitate to get in touch with us. We are eager to support you.

On behalf of the Food & Agriculture Team of Analytik Jena, I hope you enjoy reading this e-book.

Dr. Christine Marion Gräfe, Team Leader Food and Agriculture

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Challenge

Fully automated, fast and accurate determination of different chlorine parameters (TCl, TICl, TOCl) in different types of palm oil.

Solution

Organic Elemental Analysis - Matrix- and time optimized combustion with flame sensor technology using the multi EA 5100.

Determination of Different Chlorine Parameters in Palm Oil with the Elemental Analyzer multi EA 5100

Introduction

Palm oil and palm kernel oil production has grown drastically in the last 50 years. With more than 30%, it is the largest contributor to global oil and fat production. Traditionally the food and cosmetics industries are amongst the main consumers with a share of 70% of the world palm oil production, followed by usage for biofuel production. Palm oil is used in products like margarine, oil, spreads, chocolate, cleaning agents, cosmetics, candles, and many more. To improve taste characteristics and shelf life palm oil needs to be refined. But refined palm oil can pose a health risk to consumers.

Various studies carried out during the last years have proven the presence of 3-monochloropropane-1,2-diol (3-MCPD) fatty acid ester in refined palm oil. 3-MCPD is formed when fats and oils are exposed to high temperatures, in the presence of organic and inorganic bound chlorine, which often happens during the refining process. 3-MCPD is suspected to raise the risk of cancer. Experiments have shown that higher uptake of 3-MCPD triggers kidney and liver damage and benign tumors. That is why the World Health Organization has set a threshold level for the tolerable daily intake of 3-MCPD at 2 µg/kg body weight.

Used as a food ingredient, palm oil is subject to strict quality and food safety controls. Besides the determination of antioxidants, water content or trace metals (Pb, As, Cd, and Hg) also the determination of total chlorine plays an important role. Perfectly suited for this purpose is the organic elemental analysis, coupling oxidative combustion and micro coulometric detection, a well-established technology widely used and described in industrial standards like ASTM D4929 method B, ASTM D5808 or UOP 779.

Materials and Methods

Samples and reagents

Different Cl standard solutions, palm oil samples, and their dilutions with o-xylene have been analyzed.

- o-xylene (C_8H_{10}), puriss. p.a., (Riedel-de Haen, Art.-No.: 95662-1L)
- Isooctane (C_8H_{18}), Suprasolv®, GR for gas chromatography (Merck Art.-No.: 1.15440.1000)
- 2,4,6 trichlorophenol ($C_6H_3OCl_3$), GR for synthesis (Merck Art.-No.: 8.18469.0100)
- Calibration standard kit chlorine (0.1 – 10 mg/L) (Analytik Jena, Art.-No.: 402-889.071)
- Ultra-pure water

General sample preparation

Three different palm oil samples were analyzed. One crude palm oil, an intermediate from the production process, and two final products of high quality and purity. One is a red palm oil, a viscous red-orange liquid used as high quality cold-pressed cooking oil, and the other one is a 100% natural palm kernel oil for cosmetics production, a white-ivory paste-like solid substance. Depending on the quality of raw material, production method, and level of treatment, the homogeneity of palm oil samples differs, which has an effect on the reproducibility of results.
Due to the fact that the proportion of the chlorine-containing compounds in such matrices is also inhomogeneous, a sufficient pre-treatment strategy is crucial to ensure reliable measurement results.

That's why two different strategies were applied to prepare homogeneous sample aliquots. First, the samples were diluted 1:3 (w/w) with o-xylene. Second, they were carefully melted while gently shaking in a water bath, shortly before sampling. For this purpose, closed vials were used to avoid evaporation losses of the Cl-containing components. A third, very convenient type of "sample handling" is the use of an automatic sampler with integrated heating function for the sample tray and the dosing syringe. Here, the palm oil samples are tempered at slightly increased temperature, automatically by the system, so that dilution or external melting are not necessary. Thanks to the temperature-controlled dosing syringe, the sample can be dosed directly and reproducibly into the analyzer. The temperatures used can be flexibly adapted to the requirements of the respective sample.

Separation of inorganically-bound chlorine

In some cases it is very helpful to have additional information with regards to the type of Cl-compound. This helps to find possible sources of contamination and to better predict the risk potential of a palm oil during production process.
Therefore, water extraction is perfectly suited due to its simplicity and low effort. This method is recommended for low viscosity, non-asphaltene, and non-bituminous crude materials. For effective extraction, especially when expecting high inorganic Cl load, a 3:1 water/sample ratio is recommended. Two different approaches are applicable for extraction of the palm oil samples.

Extraction by centrifugation

A 3:1 water/sample mix is prepared. Therefore, 25 mL of the crude sample are filled into a centrifuge vessel of suitable capacity, then 75 mL of approx. 60 °C warm ultra-pure water is added before the vessel is closed with a cap. This sample/water mix is shaken vigorously (~ 3,000 rpm) for two minutes by aid of a centrifuge. Periodically degassing the sample by venting the cap will prevent gas buildup. In case a heated centrifuge is used, the sample/water mix, is centrifuged with appropriate counterbalance, for ten minutes. This will effectively remove particulates and the inorganic chlorides from the organic phase (crude sample) into the water phase (water extract). After sufficient time for phase separation, aliquots of both phases are pipetted carefully for Cl analysis, making sure to take the sample from the middle of each phase without picking up contamination from the other phase.

Extraction by separatory funnel

25 mL of crude sample are filled into a separatory funnel, 75 mL of ~ 60 °C warm ultra-pure water is added. In the case of solvent-diluted crudes, 50 mL of the crude/solvent mix and 150 mL of ~ 60 °C warm ultra-pure water is used instead. The separatory funnel is capped before shaking it vigorously for two minutes. Periodically degassing the sample by venting the cap will prevent gas buildup. The sample/water mix needs approx. 10–15 minutes undisturbed for sufficient phase separation. The water sample is drained from the bottom of the separatory funnel for Cl analysis.
Independent of the extraction method used, it is important to make sure no particulates are present before analyzing the water extract. If necessary it can be filtered.

Instrumentation settings

A multi EA 5100 in horizontal operation mode, including the flame sensor technology, was used for the analysis.
For sample feeding the automatic boat drive in combination with the multi matrix sampler – MMS was used. In solids mode the undiluted samples were introduced directly by means of sample boats. In liquids mode 100 µL of the diluted samples resp. the liquid standards were injected by means of a µL-syringe.
The sample digestion is carried out by efficient catalyst-free high temperature combustion in a quartz reactor. This process is controlled and adopted to the special needs of every matrix component fully automatically thanks to the flame sensor technology. This ensures matrix-independent, optimal results in the shortest possible time. The process is split into two phases. In the first phase, evaporation of light components and pyrolysis of the heavier ones takes place within an inert argon atmosphere. The resulting gaseous products are converted in the pure oxygen atmosphere of the combustion zone. In the second, phase the system switches completely to oxygen and the remaining components are combusted quantitatively.
The implemented auto protection system guarantees highest operational safety (particle and aerosol trap) and a complete transfer (no condensation loss) of the formed HCl into the titration cell. Afterwards, the determination of the chlorine content is carried out by means of micro-coulometric titration. The multi EA 5100 enables a wide operation range from 10 wt-% down to the detection limit of 50 µg/L Cl.

Method parameters

Standard method settings for the horizontal operation mode are applied. The combustion process parameters are shown in Table 1 and the TCl detection parameters in Table 2.

Table 1: Process parameters

Parameter	Specification
Furnace temperature	1050°C
2nd combustion	60 s
Ar flow (1st phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (2nd phase)	200 mL/min
Purge[1]	100 s
Draw up[2]	1 µL/s
Injection[2]	3 µL/s

[1] for the solids method only, [2] for the liquids method only

Table 2: Detection parameters

Parameter	Specification
Max. integration time	1200 s
Threshold value	300 cts
Max. drift	100 cts/s
Threshold	25 cts
Cell temperature	23 °C
Titration delay	30 s

Calibration

Liquid calibration standards based on 2,4,6-trichlorphenol in isooctane were used to calibrate the analysis system in the concentration range from 0.1 to 5 mg/L TCl. The calibration curve is shown in Figure 1. The calibration was checked with a certified reference standard.

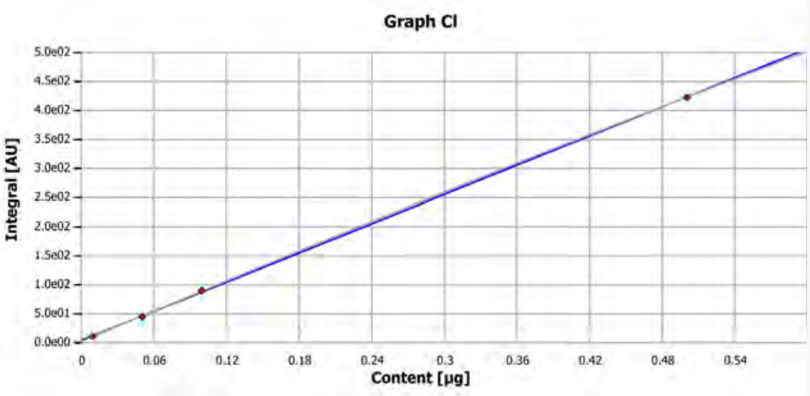

Fig. 1: Calibration curve for the TCl determination

Results and Discussion

The two different palm oil samples were analyzed twice – first directly, using the solids mode, and second in liquids mode, diluted with o-xylene. The results and the measurements of two selected Cl standards are summarized in Tables 3 (undiluted) and 4 (diluted). The results are averages of three replicate analyses. Typical measuring curves are shown in Figures 2 (undiluted) and 3 (diluted).

Table 3: Results of TCl determination in undiluted palm oil using the solid method

Measurement	TCl	RSD	Sample quantity
Red palm oil	1.27 mg/kg	± 5.95%	~ 55 mg
White palm oil	3.03 mg/kg	± 25.7%	~ 25 mg
TCl standard 1.45 mg/kg	1.49 mg/kg	± 0.29%	100 µL

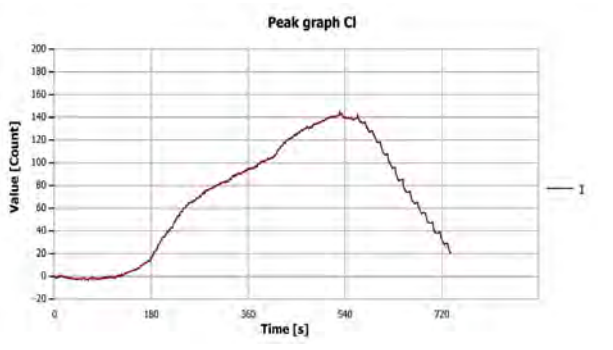

Fig. 2a: TCl measuring curve for the undiluted red palm oil

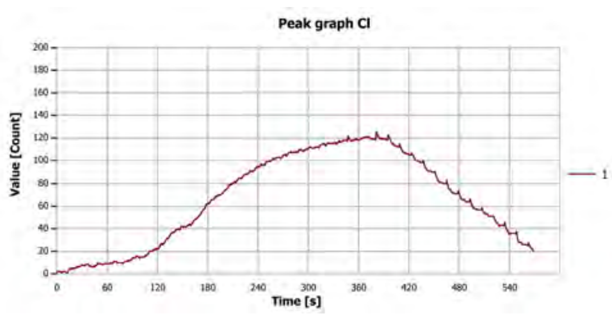

Fig. 2b: TCl measuring curve for the undiluted white palm oil

Table 4: Results of TCl determination in diluted palm oil samples

Measurement	TCl	RSD	Dilution [g in g]
red palm oil	1.30 mg/kg	± 1.99%	3.5559 in 7.3622
white palm oil	3.16 mg/kg	± 2.91%	3.4382 in 8.1002
TCl standard 0.72 mg/kg	0.71 mg/kg	± 0.54%	-

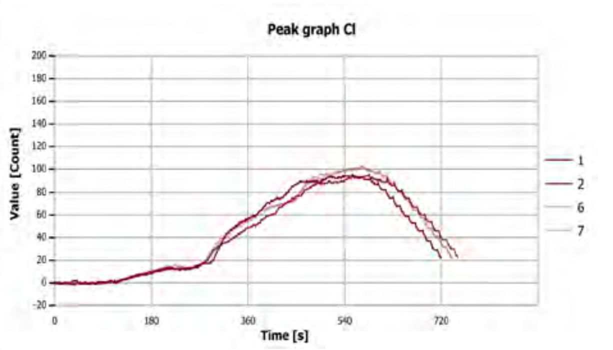

Fig. 3a: TCl measuring curves for diluted red palm oil

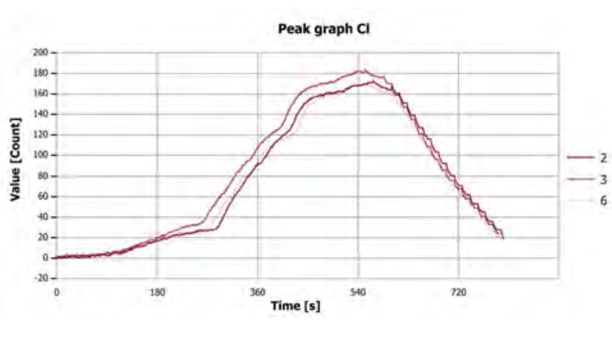

Fig. 3b: TCl measuring curves for diluted white palm oil

The different pre-treatment strategies deliver comparable results with deviations of less than 5%, thus demonstrating the general suitability of both principles for analysis of diverse palm oil samples.
Nonetheless, using dilution leads to smaller deviations of the single analyses. This as well as the easier sample handling and faster processing make the dilution strategy the superior one.

Speciation of inorganic and organically bound Chlorine

In some cases it is very helpful to have additional information with regards to the type of Cl-compound. This helps to find possible sources of contamination and to better predict the risk potential of a palm oil during processing.
The way to do this, a water extraction, is well established for oils and other not water-soluble organic samples.
In this study, the samples have been extracted manually before determination of total inorganic-bound chlorine (TICl). Therefore, the separatory funnel method was applied.

The water extracts thus prepared are analyzed quickly by aid of a cell direct method, that means direct injection of the water extract into the titration cell. This only gives result for ionic chlorine, no falsification by soluble organic matter.
Depending on the analytical task, the organically bound Cl (TOCl) can either be calculated from the known TCl content or measured from the organic phase via combustion followed by coulometric titration.

Table 5: Results for the determination of chlorine species in crude palm oil

Parameter	Concentration	RSD
TICl	10.6 mg/kg	± 0.72%
TOCl	1.22 mg/kg	± 2.68%
TCl	11.8 mg/kg	± 0.92%

For the crude palm oil sample, the total chlorine content as well as its proportions of inorganic and organically bound chlorine were measured directly. The results are summarized in Table 5, they are average values of three replicate analyses.

The calculated (TICl + TOCl) and the measured TCl are equivalent. This aproves the reliability of both measuring methods.

Conclusion

This work has successfully demonstrated that the multi EA 5100 (Figure 4) with ABD and flame sensor technology provides a fast, safe, and reliable solution for the analysis of chlorine traces in palm oil and related matrices. Due to the time- and matrix-optimized digestion process by means of the flame sensor, the quantitative combustion of any sample component is ensured. No formation of soot or other undesired pyrolysis products is observed. This and the efficient Auto-Protection system enable superior reproducibility even for the smallest chlorine quantities. A high sample throughput is easily achieved using the multi-matrix sampler MMS that is able to introduce solid as well as liquid sample matrices fully automatically either by quartz boats or by direct syringe injection.
Thanks to the modular design of the multi EA 5100 the user has any flexibility for later upgrades to determine other parameters like nitrogen, sulfur or carbon in different matrices like LPG and gases.

Figure 4: multi EA 5100

References
[1] EFSA CONTAM Panel (EFSA Panel on Contaminants in the Food Chain); SCIENTIFIC OPINION ON THE RISKS FOR HUMAN HEALTH RELATED TO THE PRESENCE OF 3- AND 2-MONOCHLOROPROPANE-DIOL (MCPD), AND THEIR FATTY ACID ESTERS, AND GLYCIDYL FATTY ACID ESTERS IN FOOD. EFSA Journal. 2016, 14/5, 4426, 159
[2] Bertrand Matthäus, ORGANIC OR NOT ORGANIC – THAT IS THE QUESTION, Eur. J. Lipid Sci. Technol. 2012, 114, 1333–1334

multi EA 5100
C/N/S/X Analysis

Efficiently Monitor Chlorine Contents
multi EA 5100

The multi EA 5100 is a combustion elemental analysis system for determination of Cl but also other quality-affecting non-metal elements (C/N/S). The intelligent coupling of efficient high-temperature combustion with ultra-sensitive coulometric detection enables a unique wide application range from 0.01 - 1000 µg Cl abs. Due to flexible automation possibilities a max. sample throughput can easily be reached independent of matrix type and properties.

- Regulatory compliance - work conform to the relevant international analysis standards (e.g. ASTM D4929 method B, ASTM D5808, UOP 779 etc.)
- Lowest maintenance effort ever at maximum uptime - soot-free sample combustion, efficient system protection against sample particles and acid vapors
- Fully automatic process optimization, no method adaptation/development by operator required
- Maximum safety for operator and analyzer by intelligent Self Check System and multiWin software

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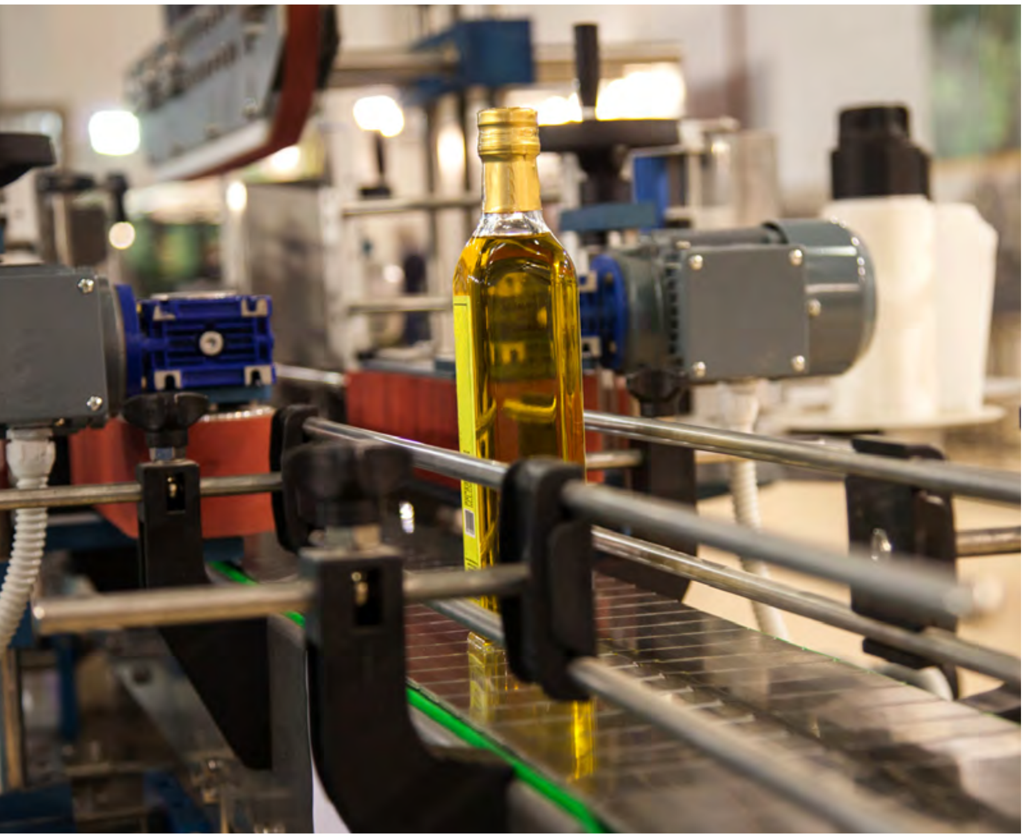
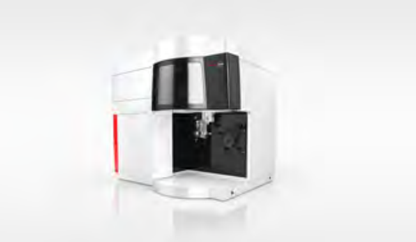




Challenge

Reliable and effective assessment of element levels in edible oils for process monitoring as well as quality and food safety control.

Solution

HR ICP-OES for the sensitive and interference-free analysis of elemental parameters relevant to processes, quality, and safety of edible oils and fats directly from solution in organic solvents.

Determination of Trace Elements and Mineral Contents in Edible Oils and Fats by HR ICP-OES

Introduction

Edible oils and fats, particularly vegetable oils, are essential for a healthy diet because they provide the body with nutrients and are low in cholesterol, rich in unsaturated fatty acids, aid in the absorption of vitamins, and act as a carrier of flavors. Oils and fats are produced from oilseeds as well as from animal sources. Today, the annual production of vegetable oils has gone up well above 200 million tons.[1] Palm, palm kernel, rapeseed, soybean, coconut, peanut, and sunflower oil are amongst the most widely used oils with the highest annual production tonnage.

Traditionally the food and cosmetics industries are amongst the main consumers of edible oils and fats. In the case of palm oil, the usage in food products uses a share of 70% of the annual palm oil production, followed by the usage for biofuels and oleochemicals. Palm oil is used in products like margarine, cooking oil, spreads, chocolate, cleaning agents, cosmetics, candles, and many more. Coconut oil has been used for cooking for thousands of years. But it also can be found in cosmetic products.

After harvesting the oilseeds, extraction methods or milling are applied to separate the vegetable oil from the seed. In the case of palm oil, a milling process separates the crude palm oil (CPO) from the palm kernel, which itself is source to produce palm kernel oil. After liberating the oil, further processing is performed in order to alter characteristics such as color, taste, odor, crystallinity, processability, and shelf life. The magnitude of processing depends on the aimed final use as well as the feedstock quality. Refining processes may contain degumming, neutralization, washing, bleaching, deodorization, and dry fractionation. These processes employ chemical alteration of oil components by glycerolysis (transesterification), interesterification, or hydrogenation. Throughout the refining process the quality of intermediates as well as final products require a thorough analytical investigation, not only to determine yield and purity of the products but also to monitor the level of trace elements that are either toxic to the human health or that have adverse effects on the quality or shelf life. Elevated levels of nickel originating from catalysts used during hydrogenation as well as iron and copper, which may originate from processing equipment or packaging, accelerate oxidation processes in the oil and therefore have tremendous effects on the shelf life of oil containing food products. Also, contents of calcium, lead, magnesium, sodium, and zinc are frequently monitored since they may reduce the process efficiency or cause inferior product quality. From a processing point of view, phosphorous containing compounds such as phosphatides need to be removed prior to the deodorization process step. Phosphorous levels above 1 mg/kg in refined and bleached oils pose the risk of catalyst poisoning as well as odd flavors in the final products and therefore need to be assessed in the according oil intermediates. Additional to quality and process control, edible oils must comply with food safety regulations concerning toxic trace elements like arsenic, cadmium, lead, mercury, and tin with maximum permitted levels in the low µg/kg range.

Accurate elemental quantification in edible oils and fats requires an analytical methodology that is sensitive and selective. Due to its multi-element determination capability (up to 70 elements), high dynamic linear range, and trace element detection capabilities, optical emission spectrometry with inductively coupled plasma (ICP-OES) is widely used for the analysis of oils and fats. The application is described in standard procedures such as ISO 105403-3, ISO 21033, and AOCS Ca 17-01.[2-4] Following these standard procedures, edible oils are diluted in low-viscous solvents (e.g., 1-butanol, kerosene, xylenes) prior to direct aspiration. In comparison to a full mineralization by ashing or digestion, this “dilute and shoot” approach provides the advantages of less sample preparation and handling, use of less equipment, and significantly reduced risk of sample handling related errors. However, the here obtained organic mixtures are challenging sample matrices to be analyzed by ICP techniques. The high load and carbon content of the organic matrix require a robust sample introduction and plasma system, which reliably excites the samples within the ICP and does not suffer from carbon build-up within the torch. Furthermore, carbon-based emission demonstrates an increased risk of spectral interferences and hence inaccurate results. In this regard, high-resolution ICP-OES analyzers offer superior peak separation as well as spectral correction models to resolve even severest interferences. A third challenge of analyzing multiple elements in edible oils via spectrometric techniques is the wide working range required to measure trace elements for food safety concerns in the same run as medium to high concentration levels of minerals and naturally existing compounds in the oils that may disturb the refining process. DualView ICP-OES systems offer an efficient investigation of traces and major levels from a single measurement without a change of setup or analysis technology.

Within this study, the performance of the PlasmaQuant 9100 Elite high-resolution ICP-OES was investigated for oil samples of different processing stages from crude oils via intermediates to final products. Sample oil specimen including palm, coconut, rapeseed, sunflower, linseed, olive, peanut, sesame, and soybean were investigated with method validation via determination of method detection limits (MDL), spike recovery testing, and long-term stability investigation.

Materials and Methods

Sample preparation

Depending on the fatty acid characteristics (e.g., chain length, degree of saturation), different oils possess different states of crystallinity, ranging from liquid via semi-crystalline to solid types at room temperature. In order to establish a uniform methodology, a solvent study was conducted prior to the analysis. Kerosene, 1-butanol, and xylenes were tested for their suitability to prepare stable measurement solutions of the here investigated oils and fats with minimum dilution factors. Standard procedures usually prefer 1-butanol over kerosene due to its better moisture tolerance and higher achievable pump rates. Since xylene has comparable physical parameters to 1-butanol, it was included in the study as well. The tests have shown that xylene is the solvent of choice for this sample type. A fivefold dilution of liquified solid samples results in mixtures which are stable for several days without any signs of crystallization. Additionally, pump rates are the same as for 1-butanol dilutions. Samples which are liquid at room temperature were diluted by a factor of two.

Prior to dilution, solid and semi-crystalline samples were liquefied by heating at a temperature of 60 °C. Stock standards and diluted samples were homogenized in an ultrasonic bath for 15 minutes. Yttrium oil-based standard (CONOSTAN, 1000 ppm) was diluted in xylenes to give a concentration of 2 mg/kg (dilution factor (DF): 5) and 4 mg/kg (DF: 2), respectively. These solutions were used on the one hand as solvent for all dilutions and on the other hand to introduce Y as internal standard.

Table 3: Instrument settings

Parameter	Standard settings	Optional settings for improved detectability and precision on K and Na
Plasma power	1450 W	1300 W
Plasma gas flow	15 L/min	
Auxillary gas flow	1.75 L/min	0.25 L/min
Nebulizer gas flow	0.35 L/min	0.30 L/min
Oxygen gas flow	0.0 L/min	0.05 L/min
Nebulizer	Concentric, 1.0 mL/min, borosilicate	
Spray chamber	Double pass cyclonic spray chamber, 50 mL, borosilicate	
Outer tube/Inner tube	Quartz/Quartz	
Injector	Quartz, ID: 1 mm	
Pump tubing	Viton (black, black)	
Sample pump rate	0.8 mL/min	
Delay time	90 s	
Torch position[1]	-3 mm	0 mm

[1] Spacing between injector and coil further supresses carbon deposits (injector tip)

Method and evaluation parameters

Table 4: Method parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Ag	328.068	axial	peak	3	3	ABC[2]	auto	Y[3]
Al	396.152	axial	peak	3	3	ABC	auto	Y
As	193.698	axial	peak	10	3	ABC	auto	CSI[4], Y
Ba	455.403	axial	peak	3	3	static	auto	Y
Ca	315.887	radial	peak	3	3	ABC	auto	Y
Cd	214.441	axial	peak	3	3	ABC	auto	Y
Cr	267.716	axial	peak	3	3	ABC	auto	Y
Cu	324.754	axial	peak	3	3	ABC	auto	Y
Hg	184.886	axial	peak	10	3	ABC	auto	CSI, Y
Fe	259.940	axial	peak	3	3	ABC	auto	Y
K[1]	766.491	radial	peak	3	3	ABC	auto	Y
Mg	280.271	radial	peak	3	3	ABC	auto	Y
Mn	259.372	axial	peak	3	3	ABC	auto	CSI, Y
Mo	202.030	axial	peak	3	3	ABC	auto	Y
Na[1]	589.592	axial/radial[5]	peak	3	3	ABC	auto	Y

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Ni	221.648	axial	peak	3	3	ABC	auto	Y
P	213.618	axial/radial[5]	peak	10	3	ABC	auto	Y
Pb	220.353	axial	peak	10	3	ABC	auto	Y
Si	251.611	axial	peak	3	3	ABC	auto	Y
Sn	189.611	axial	peak	3	3	static	auto	Y
Ti	334.941	axial	peak	3	3	ABC	auto	Y
V	309.311	axial	peak	3	3	ABC	auto	Y
Zn	202.548	axial	peak	3	3	ABC	auto	Y

[1] Optionally to be measured with oxygen addition to the plasma
[2] Automated Baseline Correction
[3] Internal standard correction using yttrium
[4] Mathematical correction of spectral interferences originating from xylenes
[5] Due to large variations in P and Na contents, the according emission lines were measured in axial as well as radial plasma observation

Results and Discussion

Palm oil is semi-crystalline, coconut oil is solid at room temperature. Therefore, a fivefold dilution in xylenes is required to obtain stable measurement solutions. Palm oil investigations included the analyses of crude palm oil as feedstock material as well as two different processing intermediates, red palm oil, and white palm oil. Achieved method detection limits (MDLs) well below 15 µg/kg ensure compliance with food safety regulations for toxic trace elements and allow for an efficient monitoring of elements that adversely affect the refining process as well as the product quality. The results of palm oil samples and crude coconut oil (see Table 5) show concentrations of elements concerning food safety which are well below the regulated limits. Quality control analysis along the palm oil refining process shows that the levels of quality indicators such as calcium, copper, iron, potassium, nickel, and sodium are reduced to sub- to low mg/kg range. Also, the removal of phosphorus containing compounds by processing steps can be effectively monitored with a level of 3.9 mg/kg in crude palm oil and 2.2 mg/kg in refined white palm oil.

Table 5: Quantitative results for investigated palm oil (PO) and coconut oil (CO) samples

Element	Line [nm]	MDL[1] [µg/kg]	Crude PO	Red PO	White PO	Crude CO	White PO Spike recovery	
			Mass fraction [mg/kg]				Spike amount [mg/kg]	Recovery [%]
Ag	328.068	1.56	0.05	0.04	<MDL	0.06	0.31	98
Al	396.152	13.0	0.72	0.55	<MDL	0.20	0.31	100
As	193.698	14.8	<MDL	<MDL	<MDL	<MDL	0.30	111
Ba	455.403	0.62	0.09	0.10	<LOD	0.03	0.31	100
Ca	317.933	5.61	25.9	20.0	0.24	4.89	0.31	101
Cd	214.441	1.03	0.06	0.06	<MDL	<MDL	0.31	98
Cr	267.716	0.86	0.04	<MDL	<MDL	<MDL	0.31	102
Cu	324.754	1.81	0.06	0.09	0.02	0.02	0.31	100
Fe	259.940	2.09	6.30	3.97	0.12	1.45	0.31	101
Hg	184.886	4.42	<MDL	<MDL	<MDL	<MDL	0.26	104
K[2]	766.491	13.1	7.93	2.51	0.17	27.7	0.31	89

Element	Line [nm]	MDL[1] [µg/kg]	Crude PO	Red PO	White PO	Crude CO	White PO Spike recovery	
			Mass fraction [mg/kg]				Spike amount [mg/kg]	Recovery [%]
Mg	280.271	0.95	6.55	2.50	0.06	12.6	0.31	101
Mn	259.372	0.42	0.83	0.35	0.03	0.19	0.31	100
Mo	202.030	3.58	<MDL	<MDL	<MDL	<MDL	0.31	99
Na[2]	589.592	14.6	3.77	1.36	0.24	3.90	0.31	91
Ni	221.648	2.94	<MDL	<MDL	<MDL	<MDL	0.31	101
P	213.618	10.3	31.7	3.85	2.20	45.7	0.31	114
Pb	220.353	8.57	<MDL	<MDL	<MDL	<MDL	0.31	99
Si	251.611	6.38	1.30	1.55	0.06	0.43	0.31	98
Sn	189.611	15.1	<MDL	<MDL	<MDL	<MDL	0.31	101
Ti	334.941	1.17	0.06	0.06	<MDL	<MDL	0.31	99
V	309.311	1.04	<MDL	<MDL	<MDL	<MDL	0.31	100
Zn	202.548	1.69	0.57	0.33	0.11	0.17	0.31	99

[1] Method-specific detection limits obtained from calibration method (DF: 5)

[2] Measured with oxygen addition to the plasma

Method validation for solid and semi-crystalline samples was performed by spiking white palm oil samples with 0.3 mg/kg of the target analytes. Spike recoveries in the range of 89% to 114% prove the accuracy of the employed method. Long-term stability was investigated on a red palm oil sample. Here a 1.0 mg/kg spike showed recoveries between 92% and 108% for an 8-hour measurement with a measurement precision of well below 2% RSD for all investigated elements (see Figure 1).

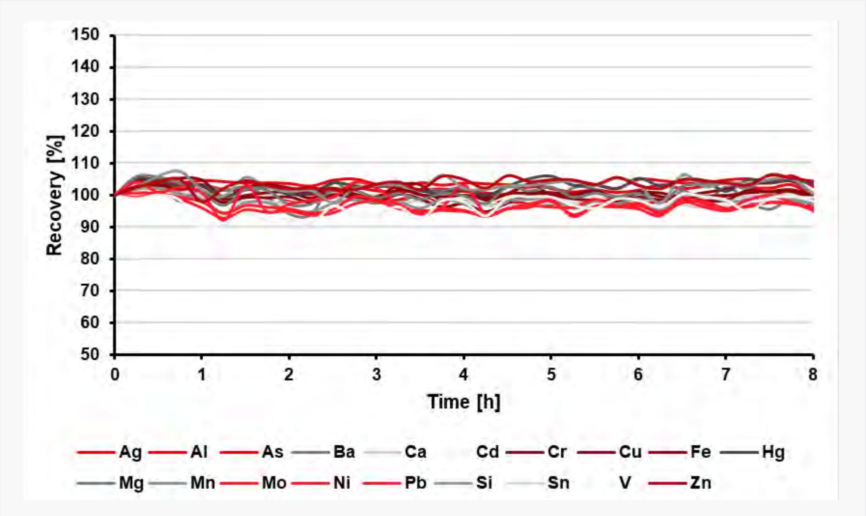


Figure 1: Percentage recoveries of an 8-hour measurement of different elements spiked (1.0 mg/kg) to diluted red palm oil. RSD values were below 1.8% for all elements

Exemplary for edible oils that are liquid at room temperature, rapeseed oil (RO) samples of different processing stages were investigated for their element concentrations. As a twofold dilution in xylenes provides a good stability of the measurement solutions, achievable method detection limits are expected to be below the ones for solid sample types. Investigating MDLs in rapeseed oil provides diverse results. Improved detectability was achieved for the majority of elements whereas some elements such as arsenic or phosphorus did not show significant improvements which may be due to the increased matrix contents originating from the lower sample dilution. Overall it can be stated that the detectability improves or shows an equal level compared to a fivefold dilution. Monitoring elements of relevance to food safety as well as to process and product quality concerns show the same behavior as the results of palm oil.

As displayed in Table 6, critical toxic elements are well below the regulated limits whereas an increased processing state of the rapeseed oil, from crude RO to refined RO, shows decreasing levels of calcium, copper, iron, potassium, nickel, and sodium. Spike recovery testing at a spike level of 0.26 mg/kg provided good recoveries in the range from 89% to 117%.

Table 6: Quantitative results for investigated rapeseed oil (RO) samples

Element	Line [nm]	MDL[1] [µg/kg]	Crude RO	Bleached RO	Half-refined RO	Refined RO	Refined RO Spike recovery	
			Mass fraction [mg/kg]				Spike amount [mg/kg]	Recovery [%]
Ag	328.068	0.83	<MDL	<MDL	<MDL	<MDL	0.27	87
Al	396.152	22.6	0.16	0.05	0.05	<MDL	0.27	91
As	193.698	15.7	<LOD	<LOD	<LOD	<MDL	0.27	111
Ba	455.403	0.28	0.03	<MDL	<MDL	<MDL	0.27	94
Ca	317.933	1.58	58.6	0.57	0.290	0.20	0.96	114
Cd	214.441	0.34	<MDL	<MDL	<MDL	<MDL	0.27	93
Cr	267.716	0.46	<MDL	<MDL	<MDL	<MDL	0.27	93
Cu	324.754	0.67	0.01	0.003	<MDL	<MDL	0.27	87
Fe	259.940	1.31	0.57	0.03	0.01	<LOQ	0.27	93
Hg	194.159	6.09	<MDL	<MDL	<MDL	<MDL	0.27	102
K[2]	766.491	26.4	28.2	0.18	<MDL	<MDL	0.96	118
Mg	280.271	0.66	11.9	0.13	0.10	0.09	0.96	93
Mn	259.372	0.10	0.17	<MQL	<MDL	<MDL	0.27	95
Mo	202.030	1.49	<MDL	<MDL	<MDL	<MDL	0.27	92
Na[2]	589.592	7.55	0.14	<MDL	<MDL	<MDL	0.27	117
Ni	221.648	0.93	<MDL	<MDL	<MDL	<MDL	0.27	94
P	213.618	11.3	164	2.92	0.66	0.48	0.27	97
Pb	220.353	8.08	<MDL	<MDL	<MDL	<MDL	0.27	92
Si	251.611	2.05	0.18	<MDL	<MDL	<MDL	0.27	85
Sn	189.611	3.71	<MDL	<MDL	<MDL	<MDL	0.27	100
Ti	334.941	1.13	<MDL	<MDL	<MDL	<MDL	0.27	93
V	309.311	0.43	<MDL	<MDL	<MDL	<MDL	0.27	93
Zn	202.548	0.49	0.20	<MDL	<MDL	<MDL	0.27	93

[1] Method-specific detection limits obtained from calibration method (DF: 2)

[2] Measured with oxygen addition to the plasma

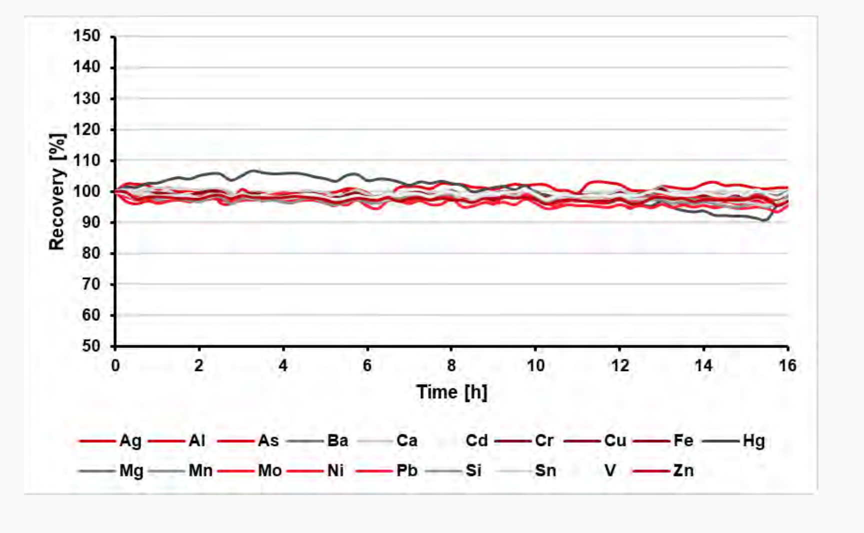


Figure 2: Percentage recoveries of a 16-hour measurement of different elements spiked (1.0 mg/kg) to diluted commercial rapeseed oil. RSD values were below 1.5% for all elements

Long-term stability testing showed recoveries between 92% to 108% for a 16-hour measurement with a measurement precision of well below 2% RSD for all investigated elements (see Figure 2).

The here developed and validated methodology can be easily extended to other edible oils such as linseed, olive, peanut, sesame, and sunflower oil, which are all liquid at room temperature. Hence, a twofold dilution of the samples can be employed for the measurement against the calibration performed for rapeseed oil. The results for seven commercially available oils are shown in Table 7.

Table 7: Quantitative results for investigated commercial vegetable oils

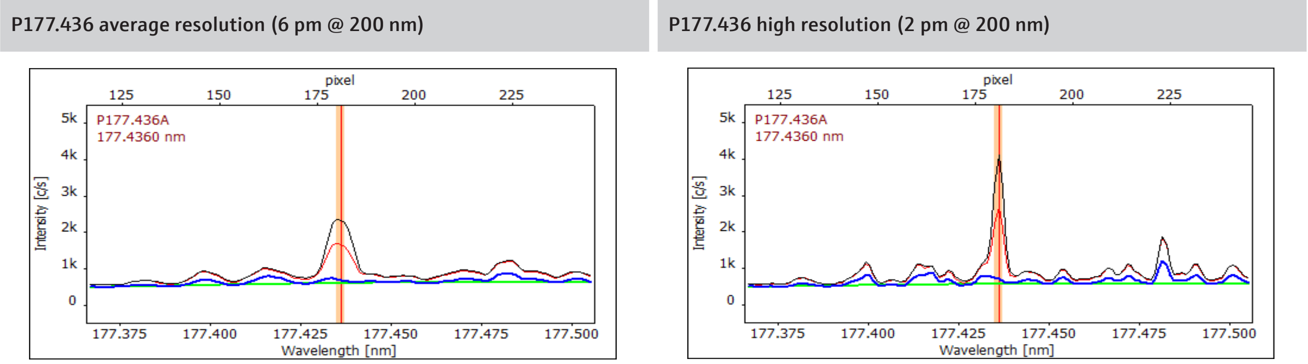
Element	Line [nm]	MDL[1] [µg/kg]	Linseed oil	Olive oil #1	Olive oil #2	Peanut oil	Sesame oil	Soybean oil	Sunflower oil
			Mass fraction [mg/kg]						
Ag	328.068	0.83	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Al	396.152	22.6	0.13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
As	193.698	15.7	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Ba	455.403	0.28	0.07	0.01	0.01	0.13	0.01	0.07	0.004
Ca	317.933	1.58	57.4	0.06	0.14	10.4	0.20	11.6	1.93
Cd	214.441	0.34	<MDL	<MQL	<MDL	0.002	<MDL	<MDL	<MDL
Cr	267.716	0.46	<MDL	<MDL	<MDL	0.002	0.002	0.01	<MDL
Cu	324.754	0.67	<MDL	<MQL	<MQL	0.01	<MDL	0.002	<MDL
Fe	259.940	1.31	0.34	<MLD	0.04	0.20	<MQL	0.49	0.02
Hg	194.159	6.09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
K[2]	766.491	26.4	19.2	<MDL	<MDL	29.9	<MQL	8.58	<MDL
Mg	280.271	0.66	34.7	0.06	0.06	11.3	0.12	8.20	0.56
Mn	259.372	0.10	0.34	<MDL	<MDL	0.14	<MDL	0.08	0.02
Mo	202.030	1.49	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Na[2]	589.592	7.55	1.12	0.11	0.11	0.48	0.33	0.71	0.37
Ni	221.648	0.93	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Element	Line [nm]	MDL[1] [µg/kg]	Linseed oil	Olive oil #1	Olive oil #2	Peanut oil	Sesame oil	Soybean oil	Sunflower oil
			Mass fraction [mg/kg]						
P	213.618	11.3	120	0.12	0.28	62.0	0.36	33.3	2.64
Pb	220.353	8.08	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Si	251.611	2.05	<MDL	<MDL	<MDL	0.05	0.03	0.16	<MDL
Sn	189.611	3.71	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Ti	334.941	1.13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
V	309.311	0.43	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Zn	202.548	0.49	1.85	<MDL	<MDL	0.21	<MDL	0.45	0.04

[1] Method-specific detection limits obtained from calibration method (DF: 2)

[2] Measured with oxygen addition to the plasma

The use of most sensitive emission lines is a prerequisite to achieve the best analytical performance in terms of achievable method detection limits as well as high accuracy and precision for trace element detection. In complex sample types such as organic materials, spectral interferences from either the matrix itself or from main constituents may restrict the use of the most suitable lines. In this regard, a high-resolution spectrometer as used in the PlasmaQuant 9100 Elite improves the separation of analyte signal and interferent to an extend that an interference-free quantification of the most sensitive line is possible for almost all elements. In this regard, Figure 3 shows the comparison of spectral data acquired with an average resolution spectrometer (Figure 3, left) and one acquired with a high-resolution spectrometer (Figure 3, right). The high-resolution reveals a second signal as a shoulder to the phosphorous line that is unnoticed in the average resolution spectrum. This interference typically stays unnoticed on common ICP-OES instruments, which causes false positive results, especially when looking for trace element contents.



P177.436 average resolution (6 pm @ 200 nm)

P177.436 high resolution (2 pm @ 200 nm)

Figure 3: Comparison of P177.436 nm spectra acquired with average spectral resolution (left) and high spectral resolution (right (red: sample, black: spike, blue: Cal. o, green: baseline correction.

Within this method, only arsenic, manganese, and mercury showed insufficiently resolved signals on their respective primary emission lines. Here an easy to adopt spectral correction algorithm such as the CSI software tool enables the removal of severe interferences to make the desired emission lines accessible for routine measurements. Figure 4 shows the as-recorded spectrum of Mn259.372 nm (Figure 4, left) with the manganese emission line situated in a very crowded spectral environment from which an accurate baseline-fitting and peak evaluation is hardly possible. Applying a spectral correction via the CSI software algorithm results in a simple to evaluate spectrum delivering highly accurate results for a previously interfered line (Figure 4, right).

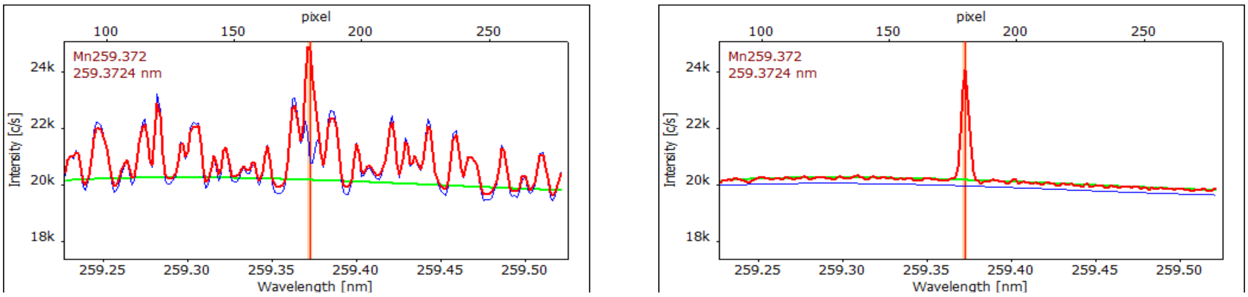

Mn259.372 (uncorrected)
Mn259.372 (CSI corrected)

Figure 4 : As-acquired spectrum of Mn259.372 nm (left) and spectrum after application of spectral corrections via CSI algorithm (right) (red: sample, black: spike, blue: Cal. 0, green: baseline correction.

In the analysis of organic sample types, emission lines in the long wavelength range suffer from elevated background levels and line-rich spectra due to carbon-based emission of the oil and solvent matrix. This mainly concerns the detectability of sodium and potassium. The resolution of the spectrometer allows for an identification of the Na589.592 nm line within a very crowded spectrum (Figure 5, left). By this it is possible to achieve detection limits in the range of 50 µg/kg, which is sufficiently low for most standard applications. However, since sodium and its removal after the neutralization process step plays a very important role in the overall process efficiency of edible oil refining, stringent monitoring of lowest levels may be beneficial to maximize the process yield.

The PlasmaQuant 9100 Elite enables the suppression of carbon-based signals in the spectrum by removing carbon in the sample feed area including the plasma. To do so, a small flow of oxygen can be dosed to convert carbon into carbon dioxide, which can easily by extracted by the ventilation of the system. The effects on the spectral complexity can be observed in the spectrum displayed in Figure 5 (right) where the background level has dropped by a factor of ten, whilst the signal to background ratio is kept the same. This allows for a tenfold increase in sodium detectability to a detection limit below 5 µg/kg. On top of this, the baseline is much smoother, and a more reliable baseline fitting can be applied with the effects of a significantly improved precision in the trace detection range.

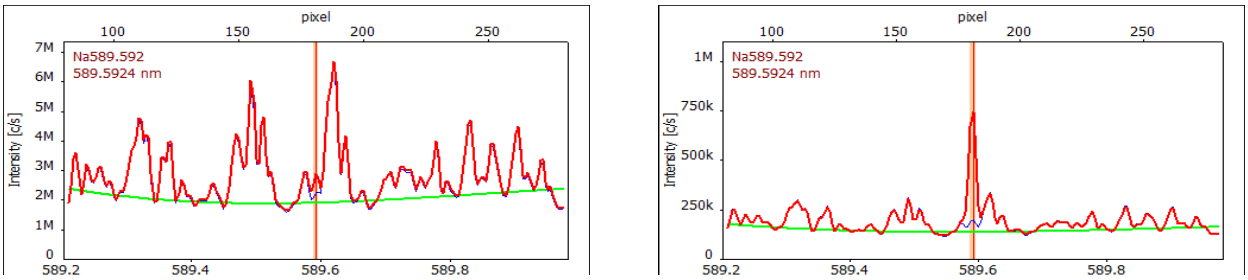

Na589.592 (regular plasma conditions)
Na589.592 (oxygen mode)

Figure 5: As-acquired spectrum of Na589.592 nm (left) and spectrum after application of oxygen (right) (red: sample, blue: Cal. 0, green: baseline correction.

Conclusion

The here presented methodology describes the analysis of elemental parameters relevant to process monitoring as well as quality and food safety control by a high-resolution ICP-OES, the PlasmaQuant 9100 Elite (Figure 6). To achieve the highest possible detectability, the approach of direct dilution of the samples in xylenes was employed since it keeps the overall dilution factors at a minimum. The challenges for the analysis of the fully organic measurement solutions are perfectly addressed by the features of the PlasmaQuant 9100 Elite, the vertical plasma orientation provided by the V Shuttle torch, the high plasma robustness by the high-frequency generator, the wide working range by the DualView Plus plasma observation modes, and the high resolution spectrometer. The results clearly demonstrate the enormous application advantages originating from the instrument features. The high-frequency generator in combination with the unique V-Shuttle torch allows for the measurement of almost any sample type including undiluted solvents and high matrix samples. Especially, the option to increase the distance of injector to the plasma offers huge advantages in daily routine of organic applications and reduces time for maintenance due to practically nonexistent carbon deposits. Furthermore, the user benefits from the possibility of operating the instrument in oxygen mode providing reduction of spectral interferences for certain elements and improving limits of detection. The high spectral resolution allows for using the most sensitive emission lines without compromises in detectability or precision in the target concentration levels. In combination with a high sensitivity and a robust plasma, exceptional limits of quantification (sub- to low µg/kg range) can be achieved with high confidence in the obtained results. Additionally, software tools such as the automatic background correction (ABC) and in particular the correction for spectral interferences (CSI) significantly reduce the time required for data evaluation and often further improve the instrument's sensitivity. In summary, the PlasmaQuant 9100 Elite is well suited for the process, quality, and food safety control of edible oils and fats.

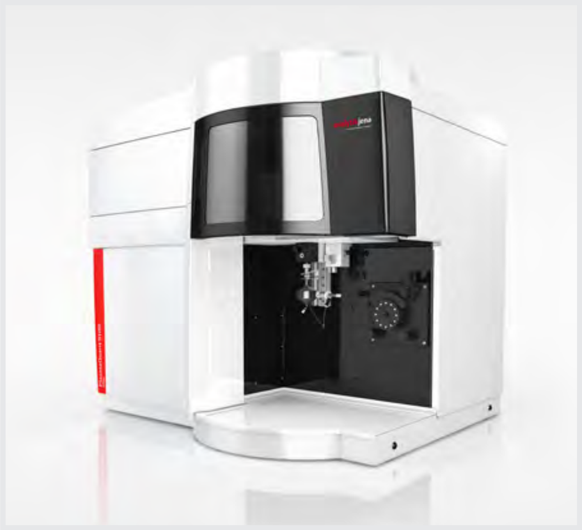


Figure 6: PlasmaQuant 9100 Elite

References
[1] Oilseeds: World Markets and Trade, United States Department of Agriculture, September 2020.
[2] ISO 10540-3, First Edition 2002/12/1, Animal and vegetable fats and oils – determination of phosphorus content; Part 3: Method using ICP-OES.
[3] ISO 21033, First Edition 2016/05/1, Animal and vegetable fats and oils – determination of trace elements by inductively coupled plasma optical emission spectroscopy (ICP-OES).
[4] American Oil Chemist Society, AOCS Recommended Practice Ca 17-01, approved 2001.

PlasmaQuant 9100
ICP-OES Analysis

Trace Element Analysis
PlasmaQuant 9100 series

ICP-OES contributes to food safety analysis as well as quality control and the monitoring of process parameters. It is a suitable technique to determine low levels of toxic elements (As, Cd, Hg, Pb), trace elements that deteriorate the quality of final oil products or perturb the refining process (Na, P). The PlasmaQuant 9100 provides a series of unique features to allow for the best analytical performance in edible oil analysis:

- Robust plasma to reliably handle organic sample types
- High-spectral resolution for interference-free and highly sensitive trace element detection
- Easy handling of torch components by unique V Shuttle Torch
- Fast system warm-up, ideal for cost-efficient shift-work operation

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Challenge

Rapid and precise quality assessment of palm oil (and other edible oils) according with 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.

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

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[2], 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 different processing stages up to refined oils allows to survey the quality gates along the value chain.

In addition to the fatty acids esterified in triglycerides, 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, the ratio between the carotene absorption at 446 nm and the corresponding value at 269 nm is an accepted indicator for the accumulation 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 to 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

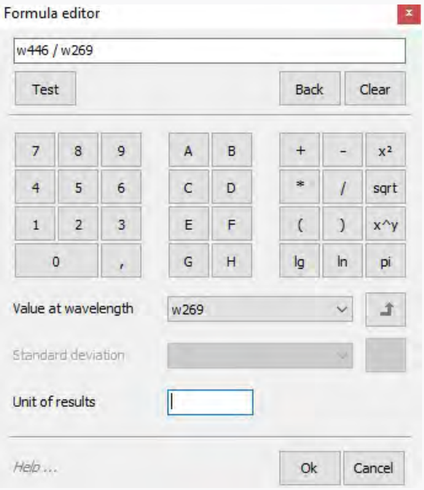
- SPECORD 50 PLUS double beam spectrophotometer is especially suited for highest spectroscopic performance and versatility towards high sample throughput,
- the ScanDrop² equipped with a Xe-flash lamp leverages operation on a small bench footprint, no warm-up time and full spectrum acquisition (220 to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

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

absorbance at the 446 nm (A_{446}) and at 269nm (A_{269}).

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).


Formula editor

w446 / w269

Value at wavelength: w269

Unit of results:

Figure 1: Formula editor of the ASpect UV software

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).

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.

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.

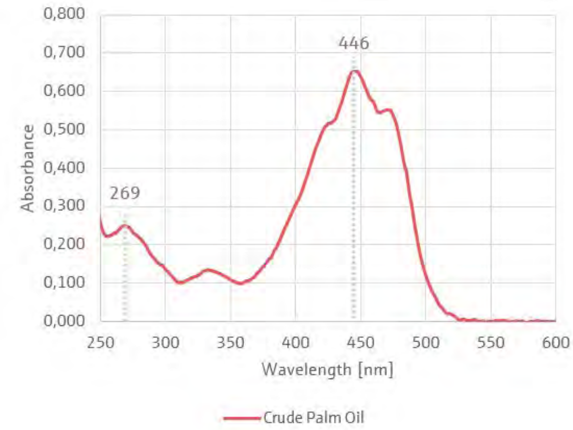


Figure 2: UV/Vis spectrum of CPO in isooctane.

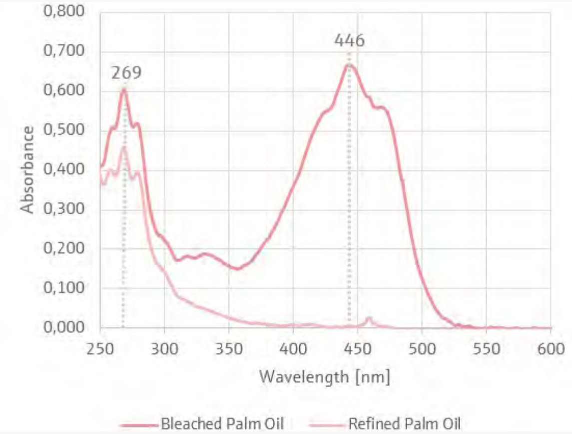


Figure 3:UV/Vis spectrum of bleached and refined palm oil in isooctane

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 2.448 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 (Figure 4) 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.

Figure 4: SPECORD 50 PLUS

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

SPECORD PLUS

UV/Vis analysis

Quantitative Insight at a Molecular Level
SPECORD PLUS UV/Vis-Spectrophotometer Series

UV/Vis spectroscopy allows quantitative and multi-parameter analysis at a molecular level, especially through rapid yet consistent evaluation of the initial raw material (crude palm oil) as well as along oil refinement and further processing of intermediate products such as bleached palm oil.

- Excellent combination of simplicity and high optical performance
- Designed for flexibility: double-beam spectrophotometer with split-beam technology and a sample chamber – from single up to multiple cuvette (6-fold or 8-fold) holders
- Reduction of the incidence of scatter light to the detector suitable for turbid samples
- Advanced and user-friendly software ASpect UV, which allows easy scan (qualitative assessment) and single wavelength probing (quantitative determination), built-in calculator, method tailoring for calibration curves, and a colorimetry module.

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In order to achieve the best possible analysis results, it is essential that instrument, accessories, consumables, and methodology are coordinated. Therefore we offer certain product configuration which are optimized for supporting you in getting reliable results in your oil analyzing process.
If you are interested in one of the product configurations given below, contact your local distributor or simply write an e-mail to **solutions@analytik-jena.com.**

multi EA 5100 (C/N/S/X analysis)

Accessories/ consumables:

- Cl module 5100
- Automatic boat drive (ABD 5100)
- Multi matrix sampler (MMS 5100)
- Extension kit Cl „high sensitive“
- Liquids kit for MMS 5100
- Standard kit for calibration and test of Cl „high sensitive“

Software/ methods

- multiWin software
- Method „Edible oil multi EA 5100“ (pre installed or file)
- SOP „edible Oil multi EA 5100“

Solid sample kit available as soon as solid samples have to be analyzed. Individual spare parts and consumables packages are available on request.

PlasmaQuant 9100 Elite (ICP-OES analysis)

Accessories/ consumables:

- Water-air-chiller for ICP
- Autosampler Cetac Oils 7400 (optional)
- ORGANIC KIT

Software/ methods

- ASpect PQ software
- Method Edible oil ICP-OES (pre installed or file)
- SOP edible Oil ICP-OES

SPECORD 50 PLUS (UV/Vis analysis)

Accessories/ consumables:

- 8-fold cuvette changer, non-temperature controlled, without stirrer
- Quartz standard cells, 10 mm pathlength, 4 pieces

Software/ methods

- ASpect UV software
- Method Edible oil UV/Vis (pre installed or file)
- SOP edible Oil UV/Vis Double Beam

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