

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 requires 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 10540-3, 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 xylenes 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.

Calibration

The here presented methodology was used to analyze a large variety of edible oil and fat samples by using an external calibration in xylenes as described in ISO 10540-3, ISO 21033, and AOCS Ca 17-01. Calibration standards were prepared from organometallic single (As: CONOSTAN, 100 ppm; Hg: CONOSTAN, 100 ppm) and multi-element standards (S21+K, CONOSTAN, 885 ppm) by diluting with xylenes using concentrations as described in Tables 1 and 2. Blank oil was used as calibration blank and was added prior to the dilution to keep the oil ratio/fraction and therefore viscosity stable within the standard solution.

Table 1: Concentration of calibration standards for the analysis of palm and coconut oils in fivefold dilution

Element	Unit	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6
Ag, Al, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Pb, Sn, Ti, V, Zn	mg/kg	0.107	0.256	0.524	1.050	-	-
As	mg/kg	0.099	0.259	0.505	-	-	-
Ca, K, Mg, P	mg/kg	-	-	0.524	1.050	5.545	10.12
Hg	mg/kg	0.098	0.256	0.508	-	-	-
Si	mg/kg	0.107	0.256	0.524	1.050	5.545	-

Table 2: Concentration of calibration standards for the analysis of vegetable oils in twofold dilution

Element	Unit	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8
Ag, Al, Ba, Cd, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Si, Sn, Ti, V, Zn	mg/kg	0.125	0.272	0.547	1.061	-	-	-	-
As	mg/kg	0.139	0.281	0.468	-	-	-	-	-
Ca, Mn, P	mg/kg	-	-	-	1.061	4.423	20.99	47.28	95.79
Hg	mg/kg	0.114	0.239	0.490	-	-	-	-	-
K	mg/kg	-	-	-	1.061	4.423	20.99	-	-
Na	mg/kg	0.125	0.272	0.547	1.061	4.423	-	-	-

Instrument settings

For the measurements a PlasmaQuant 9100 Elite ICP-OES was used in combination with a Teledyne Cetac Oils 7400 stirring autosampler. The instrument was equipped with the organic kit, comprising of a glass concentric nebulizer, a double-pass cyclonic spray chamber, a 1.0 mm id injector tube, solvent resistant tubing, and a 0.4 mL/min nebulizer.

Table 3 describes a standard set of instrumental settings which is suitable to reliably measure all elements included into this methodology. Additional to this standard setup, an optional setting, including the use of oxygen addition to the plasma, is suggested in order to achieve lowest possible method detection limits and highest possible precision for potassium and sodium in oil samples. The effects of this optimized setup are discussed below.

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: 1mm	
Pump tubing	Viton (black, black)	
Sample pump rate	0.8 mL/min	
Delay time	90 s	
Torch position[A]	-3 mm	0 mm

[A] 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 as well as 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.

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).

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

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 [%]
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
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

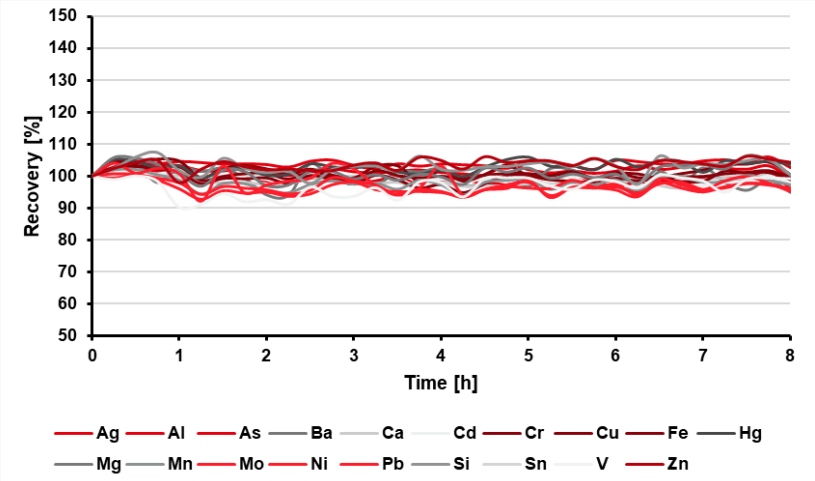


Figure 1: Percentage recoveries of an 8-hour measurement of different elements spiked (1.0 mg/kg) to diluted red palm oil. RSD values were below 1.8% for all elements

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%. 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).

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

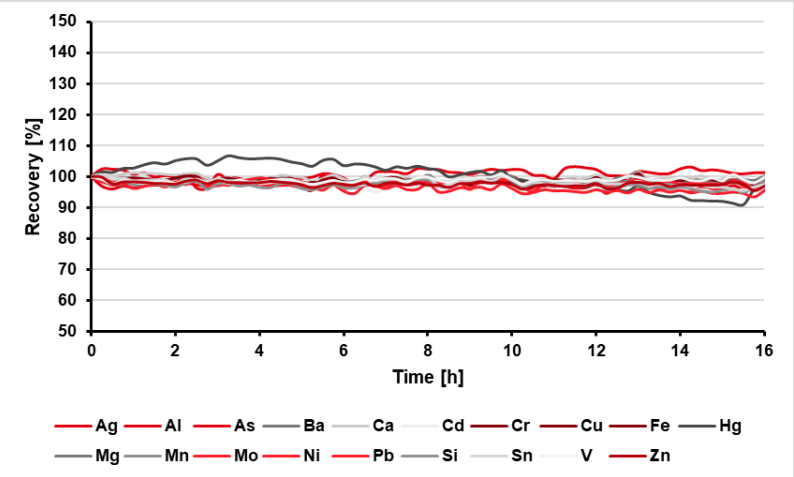


Figure 2: Percentage recoveries of a 16-hour measurement of different elements spiked (1.0 mg/kg) to diluted commercial rapeseed oil. RSD values were below 1.5% for all elements

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
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

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]						
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.

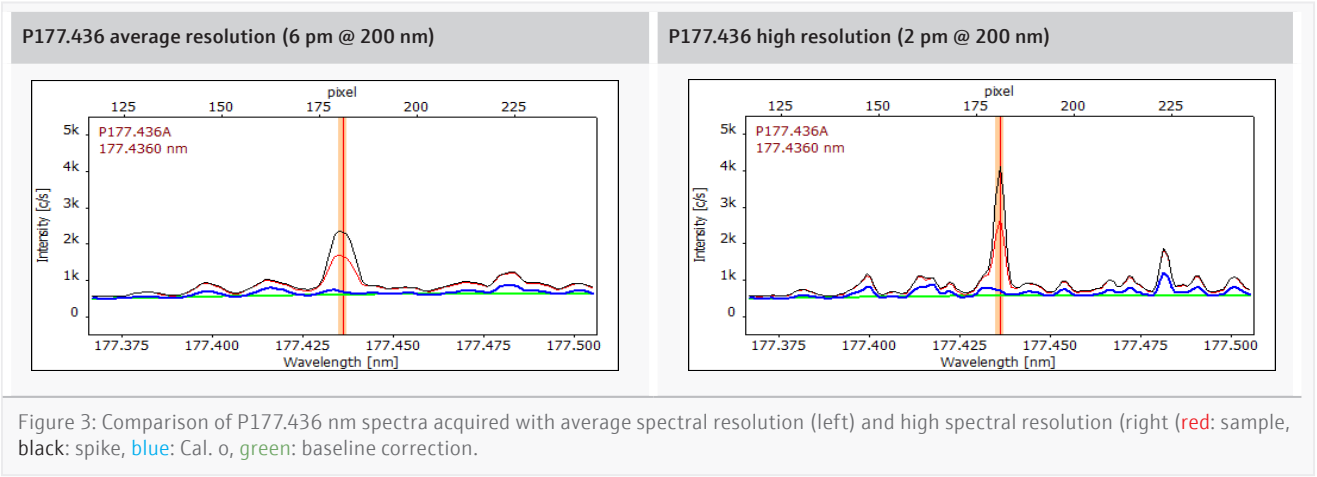


Figure 3: Comparison of P177.436 nm spectra acquired with average spectral resolution (left) and high spectral resolution (right (red: sample, black: spike, blue: Cal. o, green: baseline correction.

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).

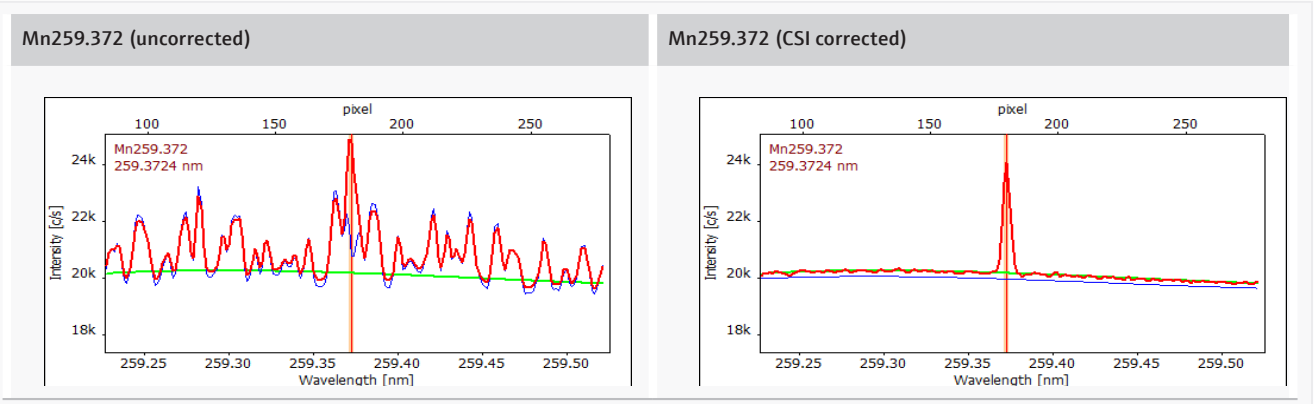


Figure 4 : As-acquired spectrum of Mn259.372 nm (left) and spectrum after application of spectral corrections via CSI algorithm (right) (red: sample, black: spike, blue: Cal. 0, green: baseline correction.

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.

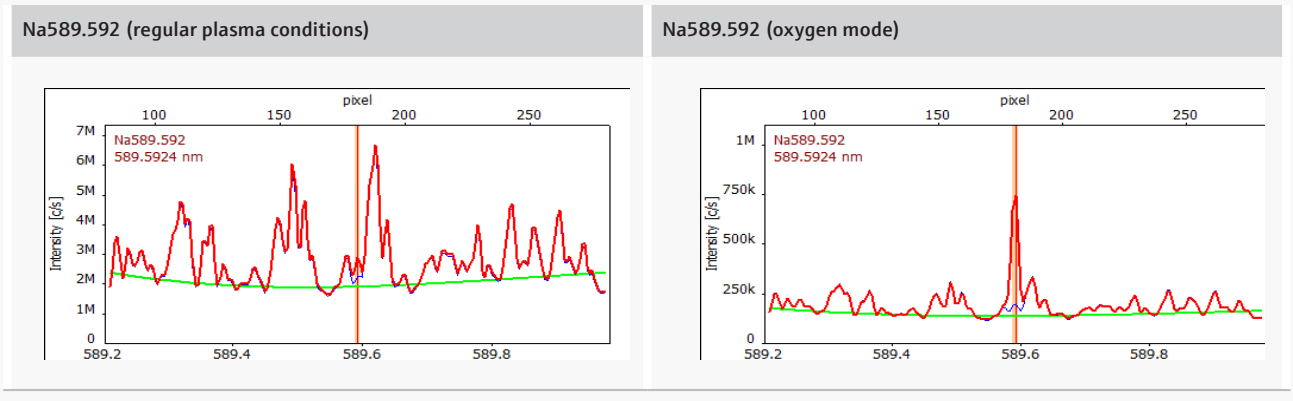


Figure 5: As-acquired spectrum of Na589.592 nm (left) and spectrum after application of oxygen (right) (red: sample, blue: Cal. 0, green: baseline correction.

Summary

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. 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.

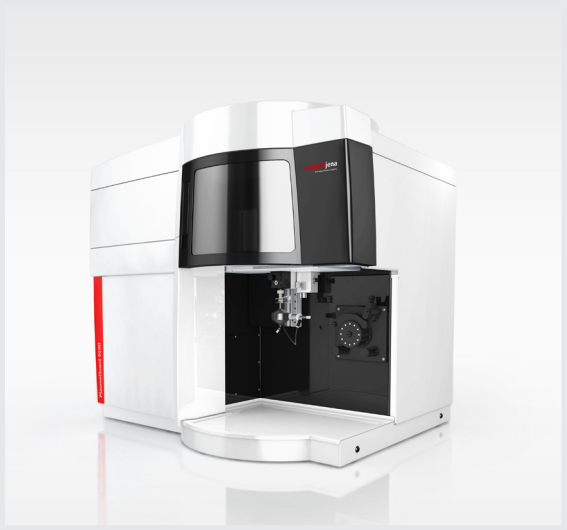


Figure 6: PlasmaQuant 9100 Elite

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[4] American Oil Chemist Society, AOCS Recommended Practice Ca 17-01, approved 2001.

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