Impurities Analysis in Sunflower Oil by HR ICP-OES

Challenge

Analysis of heavy metal impurities and macro minerals in sunflower oil from organic dilution exhibiting complex spectra due to solvent-related unspecific background signals.

Solution

HR ICP-OES with exceptional matrix tolerance towards organic matrices and high-resolution optical system in combination with a powerful software routine (CSI).

Introduction

Sunflower oil is a vegetable oil that is commonly used as main component or supplement in food, such as frying oil, salad dressing, baby food, margarine, or mayonnaise. Furthermore, it is used as an additive in cosmetics, biodiesel, varnish, textiles, and pharmaceuticals. Sunflower oil is among the most widely produced vegetable oils and is obtained from the seeds of the sunflower plant. The production includes the initial oil extraction by pressing (cold or hot) and refining processes such as solvent extraction, degumming, bleaching, and dewaxing. Refining sunflower oil increases its heat stability for frying and cooking purposes but is known to remove nutritional components (fatty acids, phospholipids, etc.), resulting in lower nutritional value and different sensory properties, such as color and flavor of the final product. Refining procedures such as transesterification or hardening aim to alter other properties, such as melting behavior, and involve the use of catalysts.

As a major constituent of food, sunflower oil is subject to many regulations concerning food safety, for example, decree 1881/2006 of the European Union, which defines limits for toxic heavy metals (e.g., Pb, Cd, Hg) in foodstuffs. On this basis, trace impurities originating from cultivation farming (fertilizers, air pollution), oil extraction, and refining processes (catalysts) need to be analyzed for purposes of food safety. At the same time, nutritional properties need to be ensured by monitoring the contents of macro minerals like phosphorus, calcium, or magnesium.

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Due to its high viscosity and potential crystallinity, sunflower oil cannot be analyzed neatly for its elemental contents. Potential methods for sample preparation are mineralization by acidic closed vessel digestion or direct dilution in a suitable organic solvent. For closed vessel digestion, only small amounts of sample can be used, which is due to the high pressures during the digestion process originating from the high carbon content of the sample. Eventually, the resulting high dilution factors compromise the limits of detection, which is a limitation for trace elemental analysis. The approach of direct dilution in an organic solvent, such as kerosene, requires only low dilution factors and therefore enables sub-ppb limits of detection in challenging sample matrices, such as sunflower oil. The fully organic sample matrix of kerosene/sunflower oil, however, requires a highly robust plasma system as well as the highest spectral resolution in order to resolve analyte lines from the extensive unspecific background signal originating from kerosene.

The methodology presented here uses a fivefold dilution of sunflower oil in kerosene that is to be investigated for arsenic, calcium, cadmium, mercury, magnesium, phosphorous, and lead on a high-resolution ICP-OES, the PlasmaQuant 9100 Elite, that is equipped with an organic sample introduction kit. The exceptionally high resolution in combination with the powerful software tool CSI (correction of spectral interferences) allows for interference-free analysis of traces of heavy metals in complex spectra featuring a high unspecific background. Furthermore, the dedicated introduction kit for organic samples in combination with the robust plasma of the HF Generator makes it possible to run 100% organic solvents with high precision and robustness.

In addition, the routine analysis of sunflower oil products largely benefit from the quality and ease of the baseline fit (ABC - automatic baseline correction), which improve precision and single-digit ppb detection limits for all elemental impurities.

Materials and Methods

Five process control samples from a sunflower oil production plant were homogenized in ultrasonic bath for 10 min and subsequently diluted with kerosene by factor 5. Calibration standards were prepared accordingly using organometallic S-21+K, As, and Hg standards (1,000 ppm; CONSTAN) and blank oil (75 cSt) in kerosene. Organometallic yttrium (1,000 ppm; CONSTAN) was used as an internal standard (IS).

Samples and Reagents

Five process control samples from a sunflower oil production plant were investigated on the PlasmaQuant 9100 Elite

Sample Preparation

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Calibration

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Table 1: Concentration of calibration standards

Element	Unit	Cal.0	Cal.1	Cal.2	Cal.3	Cal.4	Cal.5	Cal.6	Cal.7	Cal.8
As	mg/kg	0	0.0539	0.0975	0.4978	1.0032				
Ca	mg/kg						0.5013	0.9940	1.9909	4.9563
Cd	mg/kg	0	0.0539	0.0975	0.4978	1.0032				
Hg	mg/kg	0	0.0540	0.0976	0.4984	1.0044				
Mg	mg/kg						0.5013	0.9940	1.9909	4.9563
P	mg/kg						0.5013	0.9940	1.9909	4.9563
Pb	mg/kg	0	0.0539	0.0975	0.4978	1.0032				
Y[1]	mg/kg	1	1	1	1	1	1	1	1	1

[1] internal standard

Instrumentation

For the analysis, a PlasmaQuant 9100 Elite equipped with organic kit and peltier cooled spray chamber was used. The detailed system configuration is given in Table 2.

Table 2: Configuration of the PlasmaQuant 9100 Elite equipped with HF kit

Parameter	Settings
Power	1300 W
Plasma gas flow	15 L/min
Auxillary gas flow	0.5 L/min
Nebulizer gas flow	0.4 L/min
Nebulizer	Borosilicate concentric nebulizer (0.4 mL/min)
Spray chamber	IsoMist cyclonic spray chamber with dip tube, 50 mL, tempered at 20°C
Injector	1 mm, quartz
Outer tube/ Inner tube	Quartz / quartz
Pump tubing	PVC (0.76 mm ID) black/black
Sample pump rate	0.4 mL/min
Rinse/ Read delay	80 s

Evaluation Parameters

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
As	188.979	axial	peak	10	3	static	auto	Y, CSI[2]
Ca	422.673	axial	peak	3	3	ABC[1]	auto	Y, CSI
Cd	228.802	axial	peak	10	3	ABC	auto	Y, CSI
Hg	194.159	axial	peak	10	3	ABC	auto	Y, CSI
Hg	184.886	axial	peak	10	3	ABC	auto	Y, CSI
Mg	285.213	axial	peak	3	3	ABC	auto	Y, CSI
P	213.618	axial	peak	3	3	ABC	auto	Y, CSI
Pb	220.353	axial	peak	3	3	static	auto	Y, CSI
Y	371.030	axial	peak	3	3	ABC	auto	-

[1] automatic baseline fit
[2] correction by internal standard and mathematical correction of spectral interferences by CSI software tool on basis of clean kerosene spectrum

Results and Discussion

Unspecific emission lines from the kerosene-oil matrix that partly overlap the emission lines of trace elements (spectral interferences), represent a major challenge in the analysis of organic matrices. Table 4 displays the spectrum as-recorded for the sample and the pure solvent for phosphorus at 213.618 nm including its spectral environment. The comparison of spectra reveals that there is a direct overlap of an unspecific solvent signal and the sample peak, resulting in poor precision and accuracy of the obtained results. By using the CSI software tool, the spectrum of the solvent matrix can easily be subtracted from the sample signal, resulting in a simple and easy to interpret spectrum. The corresponding corrected spectrum of P 213.618 is displayed on the right hand side of Table 4. All results are summarized in Table 5. Excellent accuracy was achieved in terms of consistency testing of different analyte lines (e.g. Hg 194.159 vs. Hg 184.886) and QC recovery values between 95% and 101%. The comparison of results, in particular for the macro minerals Ca, Mg and P, reveals the expected trend: the higher the grade of processing, the lower is the nutritional value of the sunflower oil. At the same time, none of the processing steps causes elevated levels of toxic heavy metals.

Figures 1 and 2 show high-resolution spectral data for P 213.618 nm and demonstrate the applicability of the CSI tool.
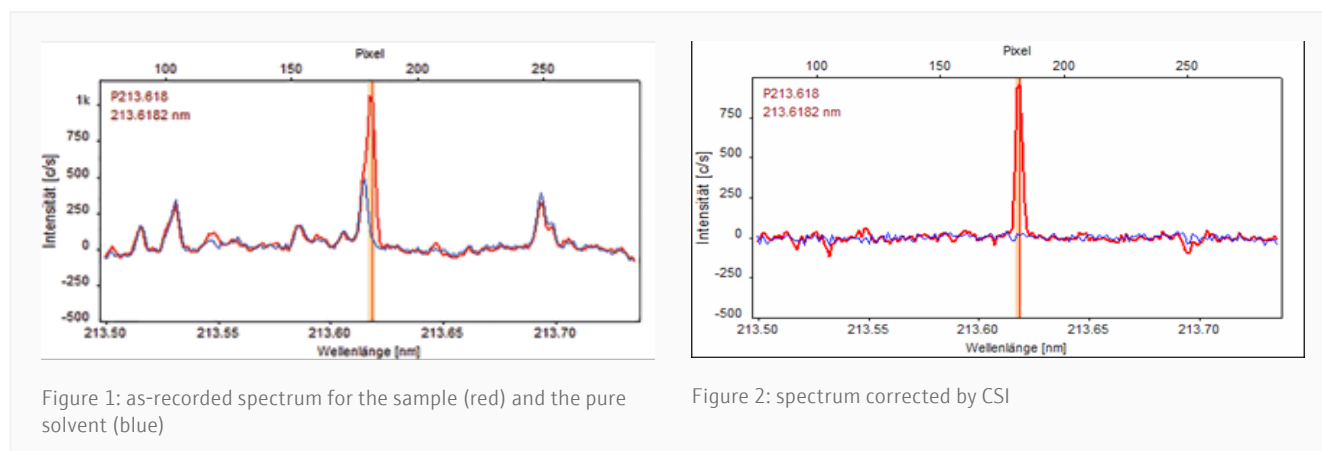

Figure 1: as-recorded spectrum for the sample (red) and the pure solvent (blue)

Figure 2: spectrum corrected by CSI

Table 5: Overview of the results for five process control samples from a sunflower production plant

Element	bleached		washed		pre-dewaxed		degummed		refined		LOD[c]	QC Cal.4 , recovery
	Result [mg/kg]	RSD [%]	Results [mg/kg]	RSD [%]	Results [mg/kg]	RSD [%]	Results [mg/kg]	RSD [%]	Results [mg/kg]	RSD [%]	[µg/kg]	[%]
As	0.0084	6.0f	0.0084	20f	0.0079	27[f]	0.0085	5.4[f]	0.0074	19f	4.28	99.6
Ca	8.03[d]	0.4	1.06	0.6	0.19	0.7	0.06	2.4	0.06	0.8	4.19	95.3
Cd	0.0016	6.4	0.0021	2.7	0.0018	4.4	0.0016	3.1	0.0014	5.6	0.19	99.3
Hg	0.018[a] (0.017)[b]	0.5	0.018 (0.016)	1.7	0.019 (0.017)	1.5	0.018 (0.017)	1.3	0.018 (0.017)	1.7	1.03 (0.32)	96.5 (95.9)
Mg	9.75[d]	1.1	0.58	0.6	0.11	1.2	0.019	1.9	0.015	0.5	0.10	98.7
P	48.0[d]	1.0	2.84	1.8	0.56	4.5	0.29	0.5	0.03	1.5	4.81	98.6
Pb	n.d.[e]		n.d.		n.d.		n.d.	1.03	n.d.		5.25	101

a values obtained for Hg 194.159 nm
b values obtained for Hg 184.886 nm
c limits of detection obtained from 3σ of SD on QC blank (11 repetitive runs) d values exceeding calibration range
e value below limit of detection
f RSD values are elevated as the content is in the sample is between the LOD and LOQ

Conclusion

Quality control of vegetable oils such as sunflower oil is a major application for food safety testing. Parameters such as levels of toxic heavy metals are as important as monitoring the levels of nutritional macro minerals. This analytical task requires a tailored sample preparation method by dilution in kerosene in order to achieve limits of detection in the low ppb range.
In this regard, unspecific emission lines from the kerosene-oil matrix that partly overlap the emission lines of trace elements (spectral interferences) are the largest concern for the precision of this analysis. Thanks to the high spectral resolution of PlasmaQuant 9100 Elite and its CSI Software tool, the interference-free analysis of all investigated elements was possible. Additionally, ease of data handling is ensured by the employment of the automatic background correction algorithm ABC.

The analysis of organic matrices requires a vertical torch concept to ensure long-term stability of the measurements. In this regard, the PlasmaQuant 9100 Elite offers the unique V Shuttle Torch, which ensures easy handling and maintenance and exceptional long-term stability for the analysis of challenging samples. Excellent method robustness was achieved by the High-Frequency Generator of the PlasmaQuant 9100 Elite and the use of a sample introduction specific to the measurement of organic matrices.

The PlasmaQuant 9100 Elite executes this analytical task from 100% organic matrix with high precision, high robustness, and low limits of detection in the ppt to ppb range. It is therefore the ideal analytical tool for routine analysis of vegetable oils.