Robust and sensitive multi-element determination in vegetable oil using ICP-OES

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Goal

To demonstrate the suitability of the Thermo Scientific™ iCAP™ PRO Series ICP-OES equipped with a ceramic D-torch for sensitive, accurate, and robust analysis of major and trace elements in food-grade vegetable oil

Introduction

Vegetable oils are widely used in foods and for cooking in most countries across the world. They tend to be favored over other oils due to their nutritional quality and lower levels of saturated fats. These oils contain trace amounts of natural elements but occasionally toxic elements from extraction processes or agricultural practices may be present (e.g., from mechanized harvesting using lead-containing fuels). There are strict regulations regarding the levels of toxic elements such as lead in vegetable oils (Table 1). Therefore, it is essential to monitor such elements in vegetable oil samples for product quality and food safety.

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) is widely used as the analytical technique of choice for the analysis of trace elements in food samples, as it allows simultaneous determination of both toxic and nutritional elements. However, when compared to aqueous samples, direct oil sample analysis using ICP-OES poses analytical challenges, such as measurement interferences from the sample matrix and more frequent maintenance due to the high carbon content of such samples. In addition, for some elements (notably phosphorus, lead, and cadmium) obtaining the required sensitivity can be challenging because the primary emission lines of these elements fall in the less sensitive ultraviolet region. Analysis of silicon is also of concern because of the high background equivalent concentrations (BEC) and drifting signal for this element generated from the ICP-OES sample introduction system over the analysis period. These issues can cause significant interferences and can affect the accuracy of trace level Si measurements.

Table 1. Maximum acceptable limits (in mg·kg^{-1}) for lead (Pb) and silicon (Si) in food samples including vegetable oil

Regulation	Maximum Pb limit in vegetable oil	Polydimethylsiloxane: $(C_2H_6OSi)_n$ maximum limitation in food stuff as additives
CODEX-standard 210-1999		-
EU EC No, 1881/2006	<0.1 mg·kg^{-1}	-
Japan Ministry Health, labor		<50 mg·kg^{-1}

Amongst target elements in vegetable oils, phosphorus and silicon are commonly analyzed as part of the quality assurance (QA) and quality control (QC) process as such elements can originate from intentionally added food additives such as antioxidants and antifoaming agents.[1,2]

This application note describes an optimized analytical method for the analysis of vegetable oil samples using the iCAP PRO Series ICP-OES equipped with a ceramic D-torch. A thorough validation of the method was performed that included analysis of quality control standards, accuracy, and precision of measurements as well as analysis of real vegetable samples as required in analytical testing laboratories.

Experimental

A Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument was used for the analysis of trace elemental concentrations in vegetable oil diluted by xylene. This instrument was selected due to its fully optimizable settings and ability to perform both Axial and Radial plasma measurements, ensuring fast sample turnaround. Mixed gas (Ar 80%, O_2 20%) was added to reduce the carbon load from aspirating organic solvent into the ICP. Viton™ peristaltic pump tubing was used to introduce the sample and remove excess sample from the spray chamber due to its resistance to xylene. A demountable ceramic D-Torch was used to minimize maintenance frequency when analyzing organic solvents and to enhance the performance for silicon analysis in such samples.

In addition, the iCAP PRO XP ICP-OES system with enhanced eUV analysis mode can further enhance the sensitivity for elements that fall in the ultraviolet wavelength range of 167.021 to 240.063 nm, such as phosphorus, lead and cadmium. The iCAP PRO XP ICP-OES system can also optimize the radial viewing height to achieve the best analysis setting. This optimization is supported by the Plasma TV feature of the instrument, allowing direct visualization of the plasma in the torch box. Details of the sample introduction setup and plasma settings can be found in Table 2. For automation of the sample introduction process, a Teledyne™ CETAC™ ASX-280 autosampler (Omaha, NE, USA) was used.

Table 2. iCAP PRO XP ICP-OES instrument parameters (optimized for organic samples)

Parameter	Setting
Pump tubing	Viton tubing
Peristaltic pump speed set	30 rpm
Torch	Duo ceramic D-torch for iCAP PRO
Centre tube size and material	1.0 mm id., quartz
Chamber	Organic spray chamber
Nebulizer	Concentric nebulizer
RF power	1,250 W
Coolant gas flow	13.5 L·min⁻¹
Aux gas flow	0.35 L·min⁻¹
Additional gas flow (Ar 80%, O_2 20%)	0.25 L·min⁻¹
Additional gas connected to	Auxiliary gas
Nebulizer gas flow	0.35 L·min⁻¹
Radial viewing height	10.0 mm
Exposure time for all modes	10 s
Up take time	20 s
Wash out time	30 s
Total analysis time (including uptake and wash out)	3 min 40 s*

*Simultaneous assessment of 112 different wavelengths

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting. The intuitive wavelength selection tool of the Qtegra ISDS Software, along with inspection of subarray plots and full frame images, was carried out to quickly select interference-free wavelengths in standard solutions. In addition, Qtegra ISDS Software was used to create the custom analysis method, selecting the eUV mode for the ultraviolet wavelength range and both view modes (Axial, Radial) in a sample analysis.

Sample preparation

Precleaned perfluoroalkoxy polymer (PFA) bottles were used for the preparation of all blanks, standards, and samples. Calibration standards were prepared by diluting oil-based standards on a weight-by-weight (w/w) basis. The stock solution used to prepare the standards was multi-element S21-K 100 mg·kg^{-1} (Conostan™, SCP SCIENCE, USA), which was diluted with xylene (Kanto Chemical Co., Ltd Japan) to final concentrations ranging from 0.2 to 1 mg·kg^{-1} (Table 3). Xylene was also used as the autosampler rinse solution.

Table 3. Concentrations of calibration solutions, QC, and sample spike recovery test

Analyte	Solution label	Concentration (mg·kg^{-1})
Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn	STD-1	0.2
	STD-2	0.5
	STD-3	1.0
	QC (CCV)	1.0
	Spike for recovery test	0.2

Approximately 4.0 g of each of the vegetable oil samples were accurately weighed and diluted to 20 g (±0.1 g) with xylene then swirled gently for 1 min.

To improve accuracy and compensate for potentially occurring instrument drift during longer sequences, internal standardization was used. Yttrium was spiked at a concentration of 1 mg·kg^{-1} to each blank, standard, or sample and used as the internal standard in the analysis.

Result and discussion

Sensitivity (LOD) and linearity

Sensitivity and linearity of the target elements were determined from the analysis of the calibration blank and solvent standards. Table 4 shows excellent linearity, with the coefficient of determination $R^2 > 0.9993$ over the calibration ranges 0.1 to 1 mg·kg^{-1}, and low limits of detection. The LODs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. The LODs for all the elements of interest are significantly below the levels required for vegetable oil sample analysis (Table 1).

Table 4. Linearity (R^2) and sensitivity (LOD as mg·kg^{-1}) data for 22 target elements determined from solvent (xylene) standards

Analyte	Wavelength [nm]	Mode	Axial		Radial	
			Coefficient of determination, R^2	LOD (mg·kg^{-1})	Coefficient of determination, R^2	LOD (mg·kg^{-1})
Ag	328.068	iFR	1.0000	0.0013	1.0000	0.0044
Al	396.152	iFR	1.0000	0.0030	1.0000	0.0112
B	249.773	iFR	0.9993	0.0017	0.9995	0.0079
Ba	233.527	iFR	1.0000	0.0006	1.0000	0.0013
Ca	422.673	iFR	0.9999	0.0024	1.0000	0.0101
Cd	214.438	eUV	0.9999	0.0002	1.0000	0.0008
Cr	283.563	iFR	1.0000	0.0006	1.0000	0.0012
Cu	324.754	iFR	1.0000	0.0008	1.0000	0.0022
Fe	259.940	iFR	1.0000	0.0009	1.0000	0.0031
K	766.490	iFR	0.9996	0.0196	1.0000	0.0515
Mg	280.270	iFR	0.9996	0.00001	1.0000	0.0002
Mn	257.610	iFR	0.9999	0.0001	1.0000	0.0005
Mo	202.030	iFR	1.0000	0.0022	1.0000	0.0075
Na	589.592	iFR	1.0000	0.0086	1.0000	0.0136
Ni	221.647	eUV	1.0000	0.0008	1.0000	0.0018
P	213.618	eUV	1.0000	0.0082	1.0000	0.0221
Pb	220.353	eUV	1.0000	0.0031	1.0000	0.0148
Si	251.611	iFR	1.0000	0.0031	1.0000	0.0091
Sn	283.999	iFR	1.0000	0.0067	1.0000	0.0247
Ti	334.941	iFR	1.0000	0.0004	1.0000	0.0011
V	309.311	iFR	1.0000	0.0008	1.0000	0.0016
Zn	213.856	eUV	0.9999	0.0014	1.0000	0.0023

Each wavelength and analysis mode used in this work is shown in Table 4. The intelligent Full Range (iFR) analysis mode can measure wavelengths between 167.021 and 852.145 nm in one simultaneous measurement; this allows for a significant reduction of the analysis times. The optional enhanced eUV analysis mode can be used to further improve sensitivity for elements that fall in the wavelength range of 167.021 to 240.063 nm.

In Figure 1, the subarray window for Si 251.611 nm, the data show that the universal ceramic D-torch provides nearly 10 times lower silicon background in xylene as compared to the quartz torch. Additionally, no signal drift was observed with the D-torch for long-term analyses of vegetable oil samples, allowing for robust and sensitive analytical results.

Superior BEC (0.002 mg·kg^{-1} in xylene) and consequently lower detection limit (0.003 mg·kg^{-1} in xylene) are shown (Figure 2).
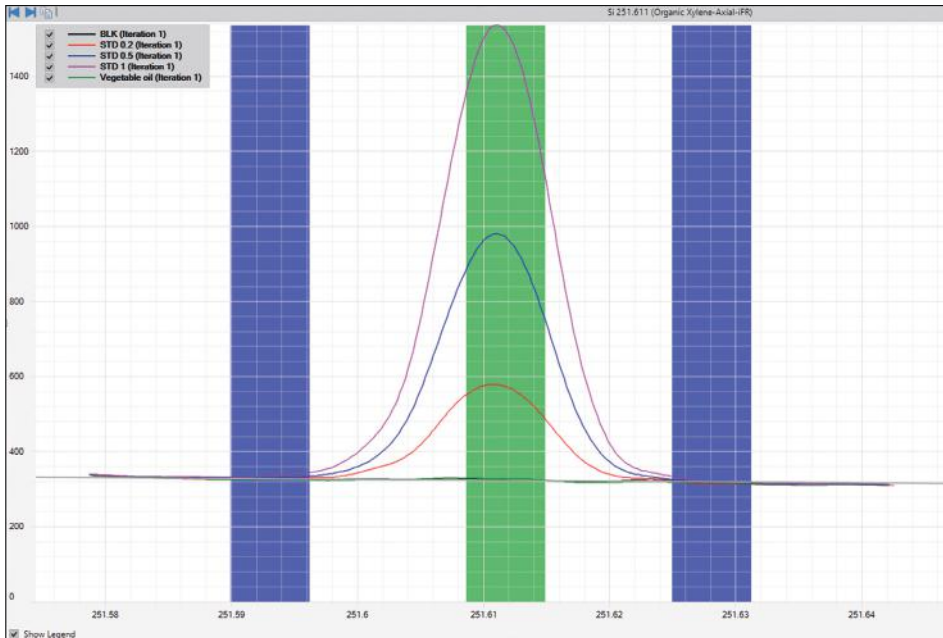

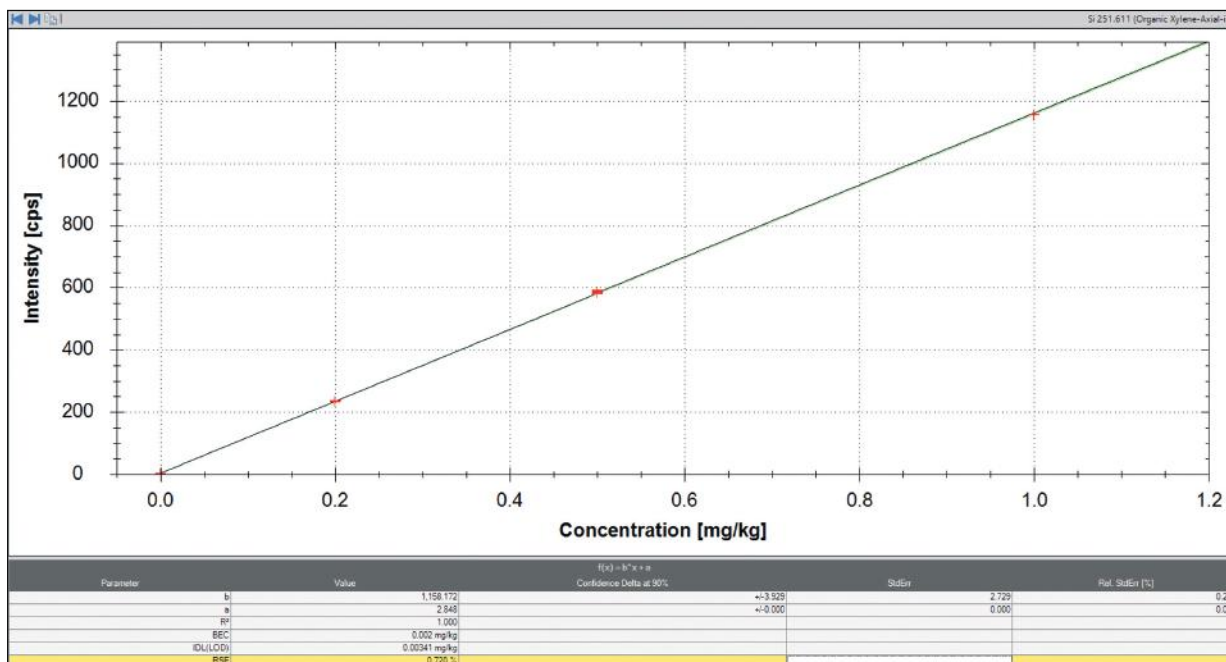Figure 1. Qtegra ISDS subarray window for Si 251.611 nm, indicating the peak center, right and left background

Figure 2. Calibration curve for Si 251.611 nm in Axial viewing mode assessed over a concentration range of 0.2–1 mg·kg^{-1}

Accuracy, precision, and robustness

For reliable analysis in an essential testing laboratory, it is important that the results obtained are accurate and precise in longer batches comprising different sample types. Commonly, spike recovery or QC standards containing a known concentration of all analytes are analyzed periodically during a sample batch to monitor method performance. To evaluate analysis precision for this analysis method, spike recovery tests were performed using vegetable oil samples spiked at 0.2 mg·kg⁻¹ for all analytes. The results demonstrate excellent accuracy with recovery values between 90% and 107% for 5-fold diluted vegetable oil samples. The RSDs (%) obtained from five replicated spiked samples were below 1%, with the exception of sodium, which was 4.5% (possibly due to contamination from the analysis environment). The results obtained for vegetable oil, spike recovery, and method detection limits (MDLs) are summarized in Table 5. MDLs are based on the instrumental detection limits summarized in Table 4 with the dilution factor of five incurred during the dilution process included.

Table 5. Quantification results for vegetable oil, spike recovery and method detection limits (MDLs)

	mg·kg⁻¹				%	
	Axial MDL	Radial MDL	Vegetable oil	Spiked mean (n=5)	Spiked (n=5) RSD	Spiked recovery
Ag	0.007	0.022	<MDL	0.20	0.38	98.95
Al	0.015	0.056	<MDL	0.19	0.79	96.62
B	0.107	0.040	0.021	0.22	0.12	107.54
Ba	0.003	0.007	0.014	0.21	0.10	101.75
Ca	0.012	0.051	0.014	0.20	0.26	97.02
Cd	0.001	0.004	<MDL	0.21	0.38	103.02
Cr	0.003	0.006	0.001	0.21	0.19	102.65
Cu	0.004	0.011	<MDL	0.20	0.15	100.61
Fe	0.005	0.016	0.002	0.20	0.33	101.62
K	0.098	0.258	0.023	0.19	0.80	93.69
Mg	0.001	0.001	0.004	0.21	0.05	103.61
Mn	0.001	0.003	0.001	0.21	0.30	102.91
Mo	0.011	0.038	<MDL	0.20	0.52	100.38
Na	0.043	0.068	<MDL	0.17	4.54	90.55
Ni	0.004	0.009	0.006	0.21	0.17	101.88
P	0.041	0.111	0.052	0.21	0.93	99.83
Pb	0.016	0.074	0.022	0.21	0.78	101.51
Si	0.016	0.046	0.058	0.21	0.28	101.43
Sn	0.034	0.124	<MDL	0.19	0.87	97.57
Ti	0.002	0.006	<MDL	0.20	0.51	102.29
V	0.004	0.008	0.002	0.21	0.21	102.61
Zn	0.007	0.012	<MDL	0.20	0.20	100.20

To evaluate robustness, a sample batch containing 51 vegetable oil samples was scheduled for analysis. Each sequence in the batch (consisting of five individual samples) was concluded with a quality control standard (continuing calibration verification (CCV), containing 1 mg·kg^{-1} of all target analytes) and internal standard signals were monitored. In summary, five CCVs were analyzed in a batch containing 51 samples in approximately 3 h using both Axial and Radial modes. Figure 3 shows the results obtained for all QC CCV samples. The relative standard deviation of all CCVs analyzed (n=5) in the batch did not exceed RSD ±0.8% for both Axial and Radial modes over 3 h, which indicates that the iCAP PRO XP ICP-OES system allows for robust and reliable long-term analysis, even for xylene.

The response of the internal standards is shown in Figure 4. The internal standard showed excellent recovery (within 94% to 103%) over the entire sample batch, demonstrating robust analytical performance with vegetable oil samples.
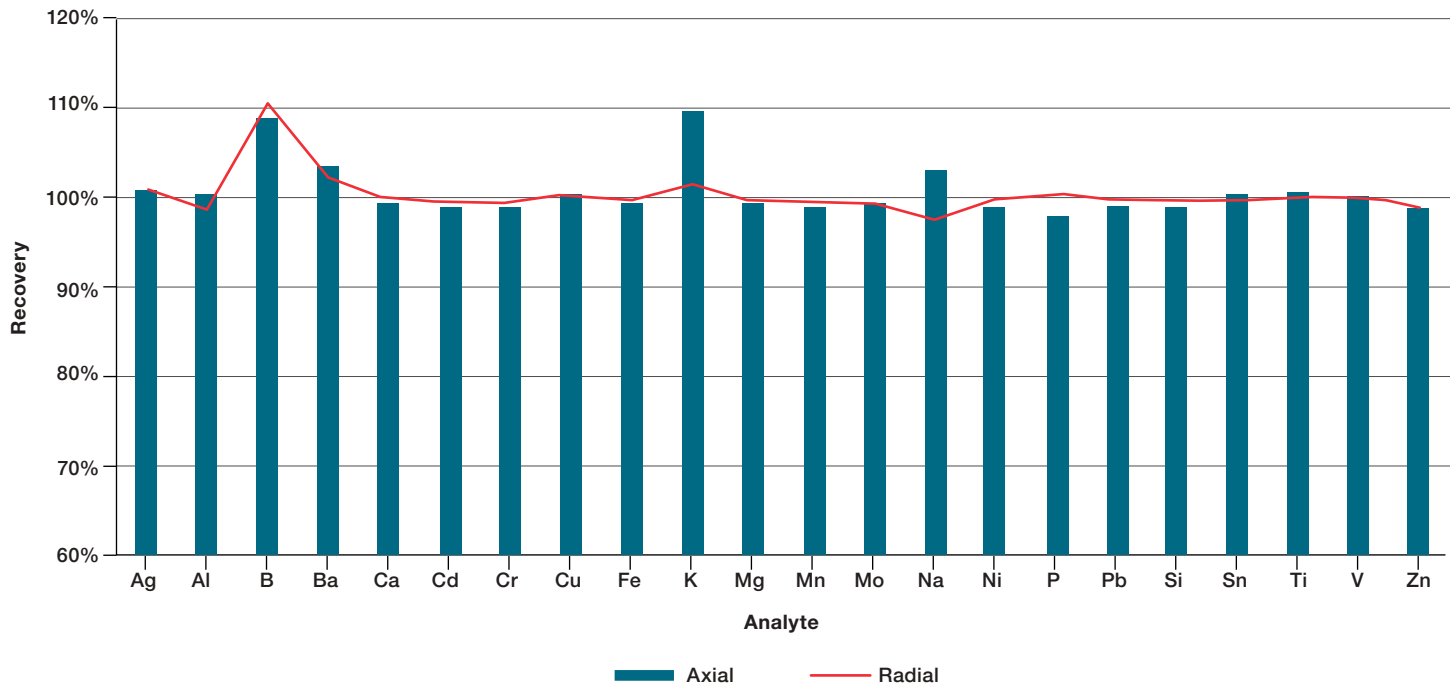

Figure 3. QC calibration verification results (n=5). CCV recovery is normalized relative to the concentration of 1 mg·kg^{-1}.
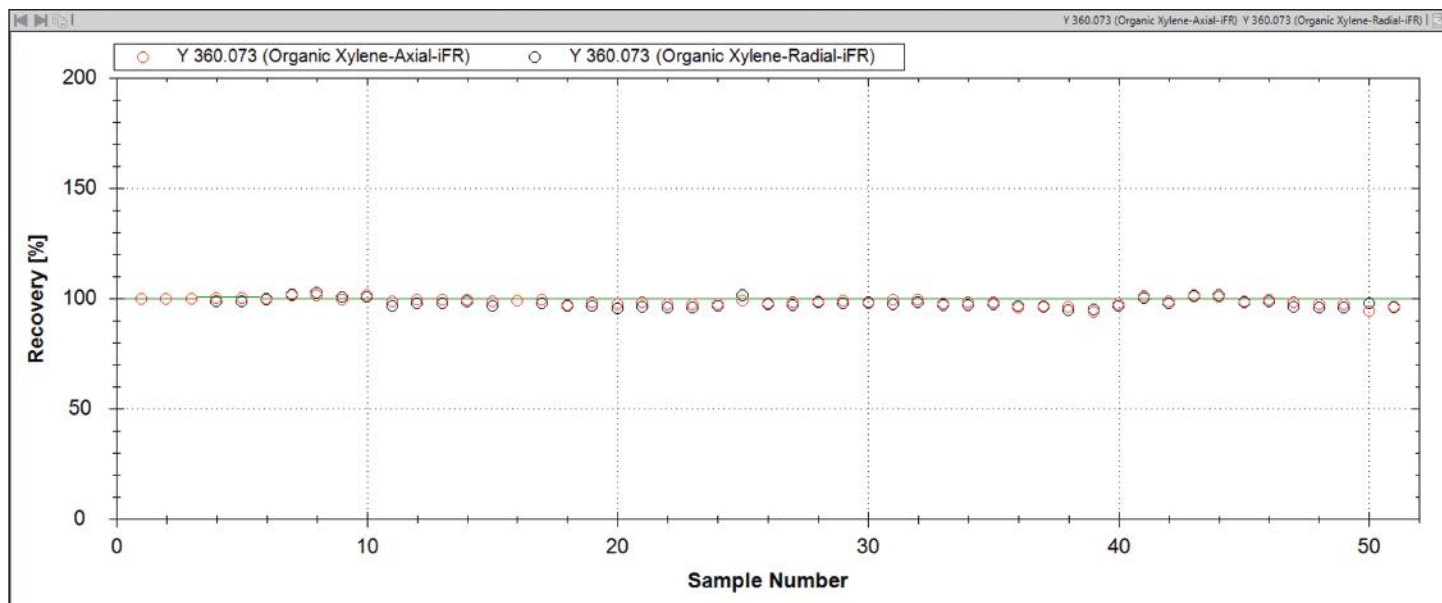

Figure 4. Response of the internal standard (yttrium) assessed over a period of ~3 h of uninterrupted acquisition of 51 samples

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Conclusion

The iCAP PRO XP ICP-OES Duo instrument equipped with a ceramic D-torch was used to analyze 22 elements in vegetable oil samples following simple, minimum dilution with xylene. Both toxic and nutritional elements were analyzed. High sensitivity, accuracy, and robust analysis were demonstrated. This analytical method was rigorously tested, and the results obtained clearly demonstrate the following analytical advantages:

- High sensitivity achieved the detection limit below 0.01 mg·kg^{-1} for all challenging ultraviolet wavelength region analytes, such as phosphorus, lead, and cadmium.

- Excellent spike recovery results (±10%) and QC CCV results (RSD ±0.8%) were obtained for vegetable oil samples, demonstrating the accuracy of the analytical technique without the necessity of maintenance.

- Excellent performance of silicon in vegetable oil samples, thanks to the significantly lower BEC of the ceramic D-torch provides compared to the standard quartz torch.

- The iCAP PRO XP ICP-OES Duo system allowed the aspiration of minimally diluted vegetable oil samples and obtained excellent MDLs.

- The iCAP PRO XP ICP-OES Duo system offers the flexibility to choose suitable analytical wavelengths and provides effective interference correction for target elemetns in a vegtable oil sample matrix.

- The flexibility of the Qtegra ISDS Software allows customization of the analytical method by enabling selection of the eUV wavelength range and both plasma viewing modes (Axial, Radial) in a sample analysis, which provides a wider range of development for analytical research.

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