Application of ICP-OES for the simultaneous analysis of nutritional and toxic metals in vegetable oils

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Abstract

Purpose: To demonstrate sensitive, accurate, and robust analysis of major and trace elements in food-grade vegetable oil using inductively coupled plasma optical emission spectroscopy (ICP-OES).

Methods: A Thermo Scientific™ iCAP™ PRO Series ICP-OES instrument equipped with a demountable ceramic D-torch was used for the analysis of vegetable oils diluted in xylene. Quality control checks and accuracy checks were performed to validate the analytical method and a sequence of about three hours length was run to check the robustness of the method.

Results: The excellent detection limits achieved in both axial and radial modes offers flexibility to choose between two viewing modes. The accuracy obtained for spiked samples were found to be in the acceptable range with excellent robustness over a period of three hours.

Introduction

Vegetable oils are amongst the most commonly and widely used fats in cooking. While their nutritional quality and relatively low saturated fat content is favorable for human consumption, the presence of contaminants and toxic components must be carefully monitored. Toxic trace metals may find their way into these oils from the processing instruments, for example. Thus, vegetable oil analysis is extremely important for human health and safety.

Strict regulations exist for elements such as lead (Pb) in vegetable oils. For e.g., 0.1 mg·kg-1 maximum lead content is permitted according to the EU EC No. 1881/2006[1], Japan Ministry of Health, Labor and Welfare[2] and other regulatory bodies globally. In this study we present a method using ICP-OES for reliable and accurate analysis of such oil samples. The method enables analytical testing laboratories to characterize trace metals in vegetable oils in compliance with regulatory limits.

Methods and materials

Test methods

A Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument equipped with a demountable ceramic D-torch, 1 mm id. quartz center tube and baffled cyclonic spray chamber (Instrument parameters in Table 1) was used for the analysis of vegetable oil samples diluted in xylene.

This application note describes an optimized analytical method for the analysis of vegetable oil samples. A thorough validation of the method was performed that included analysis of quality control standards, accuracy, and precision and robustness as required in analytical testing laboratories.

Table 1. iCAP PRO XP ICP-OES instrument parameters (optimized for organic samples.

Instrument Parameter	Setting
Pump tubing	Viton tubing
Peristaltic Pump speed	30 rpm
Torch	Ceramic D-torch
Centre tube	1.0 mm id., quartz
Spray chamber	Baffled cyclonic spray chamber
Nebulizer	Concentric nebulizer
RF power	1250 W
Coolant gas flow	13.5 L·min-1
Aux gas flow (Ar 80%, O₂ 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/mode	10 s
Uptake time	20 s
Wash time	30 s

*Simultaneous assessment of 112 different wavelengths

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Data analysis

All data acquisition and reporting in this study was done using Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Selection of interference free wavelengths was possible using the intuitive wavelength selection tool of the Qtegra ISDS Software. All steps including plasma ignition, stabilization, instrument tuning and performance check can be performed automatically from the Qtegra ISDS Dashboard without any user intervention.

Samples and standards

Vegetable oil samples (4 g) were accurately weighed into precleaned perfluoroalkoxy polymer (PFA) bottles and diluted with xylene to 20 ± 0.1 g. The diluted sample solutions were measured directly in the ICP-OES system.

The multi-element S21-K 100 mg·kg-1 (Conostan™, SCP SCIENCE, USA) was used to make standard solutions ranging from 0.2 to 1 mg·kg-1 (Table 2). The diluent used to prepare all calibration solutions, quality control (QC) standards and the autosampler rinse was xylene.

Table 2. Concentrations of analytes in calibration solutions, QC, and spiked samples. List of analytes: Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn

Calibration Solution	Concentration (mg·kg-1)
Blank	0
Std 1	0.2
Std 2	0.5
Std 3	1.0
QC (CCV)	1.0
Spike concentration	0.2

Results

Sensitivity (LOD) and linearity

Exceptionally low detection limits and wide linearity was obtained in this study for all elements as listed in Table 3. For the entire wavelength range intelligent full range (iFR) can be used which provides very good sensitivity for all analytes. Optionally, for elements with emission lines in the wavelength range of 167.021 to 240.063 nm, such as phosphorus, lead, cadmium etc. the enhanced ultraviolet mode (eUV) can be used. This provides enhanced sensitivity and improves detection limits further. All selected wavelengths within a single mode, e.g., Axial iFR, can be captured simultaneously in the same exposure (10 s in this study) reducing the analysis time.

The data in Table 3 shows the coefficient of determination R[2] was > 0.9993 over the calibration ranges 0.1 to 1 mg·kg-1. The subarray window for silicon (Si) 251.611 nm is shown in Figure 1 and the calibration curve for the same in Figure 2. The data shows that nearly 10 times lower silicon background was achieved in xylene using the universal ceramic D-torch as compared to the quartz torch. Also, superior BEC value of 0.002 mg·kg-1 and low detection limit of 0.003 mg·kg-1 were obtained for Si using this method and instrument setup.

Table 3. Sensitivity data – limit of detection (LOD) in both Axial and Radial modes

Analyte	Wavelength [nm]	Mode	Axial Coefficient of determination, R²	Axial LOD (mg·kg-1)	Radial Coefficient of determination, R²	Radial 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

LOD calculated as three times standard deviation of repeat blank runs
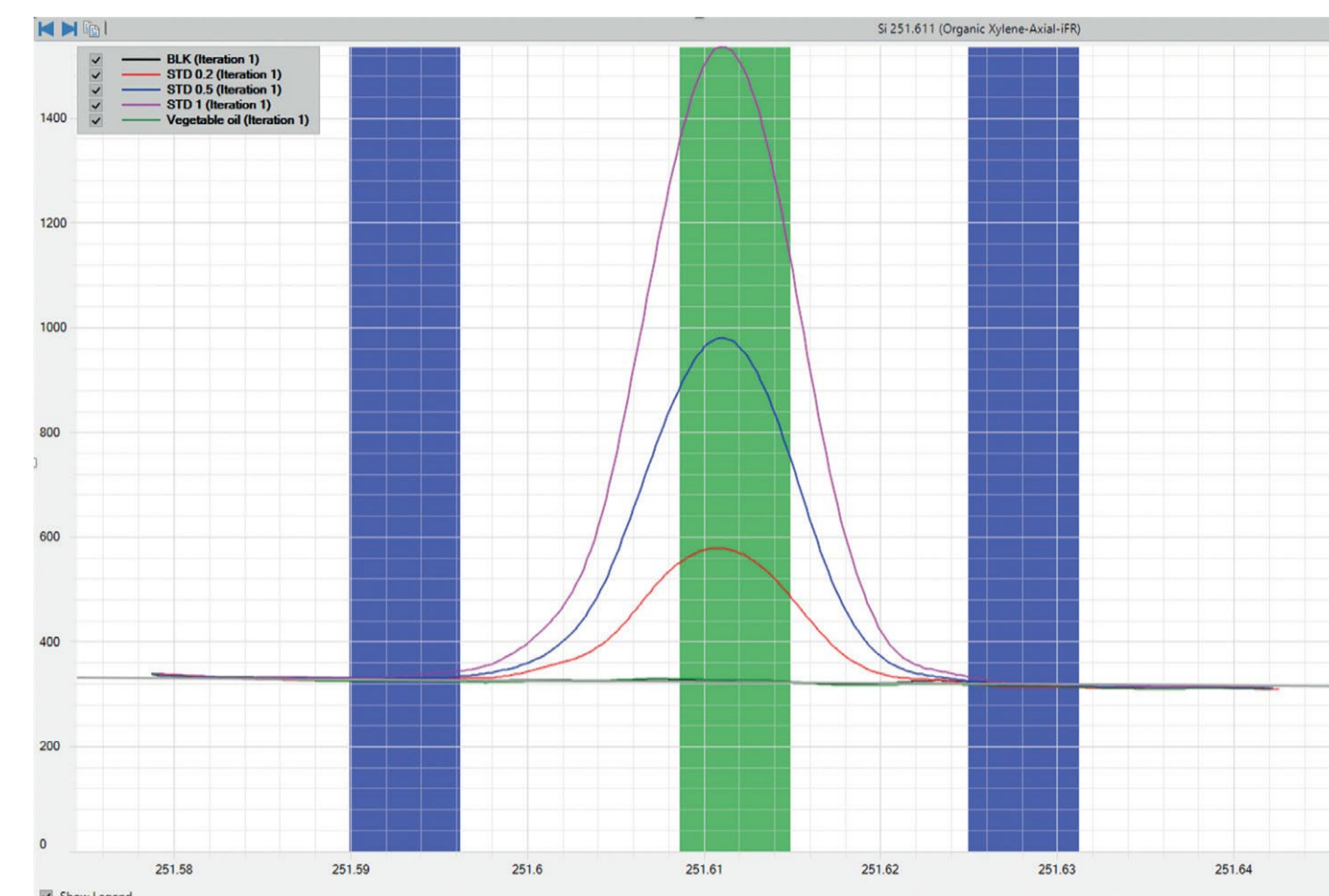
Figure 1. Qtegra ISDS software subarray window for Si 251.611 nm, indicating the peak center, right and left background
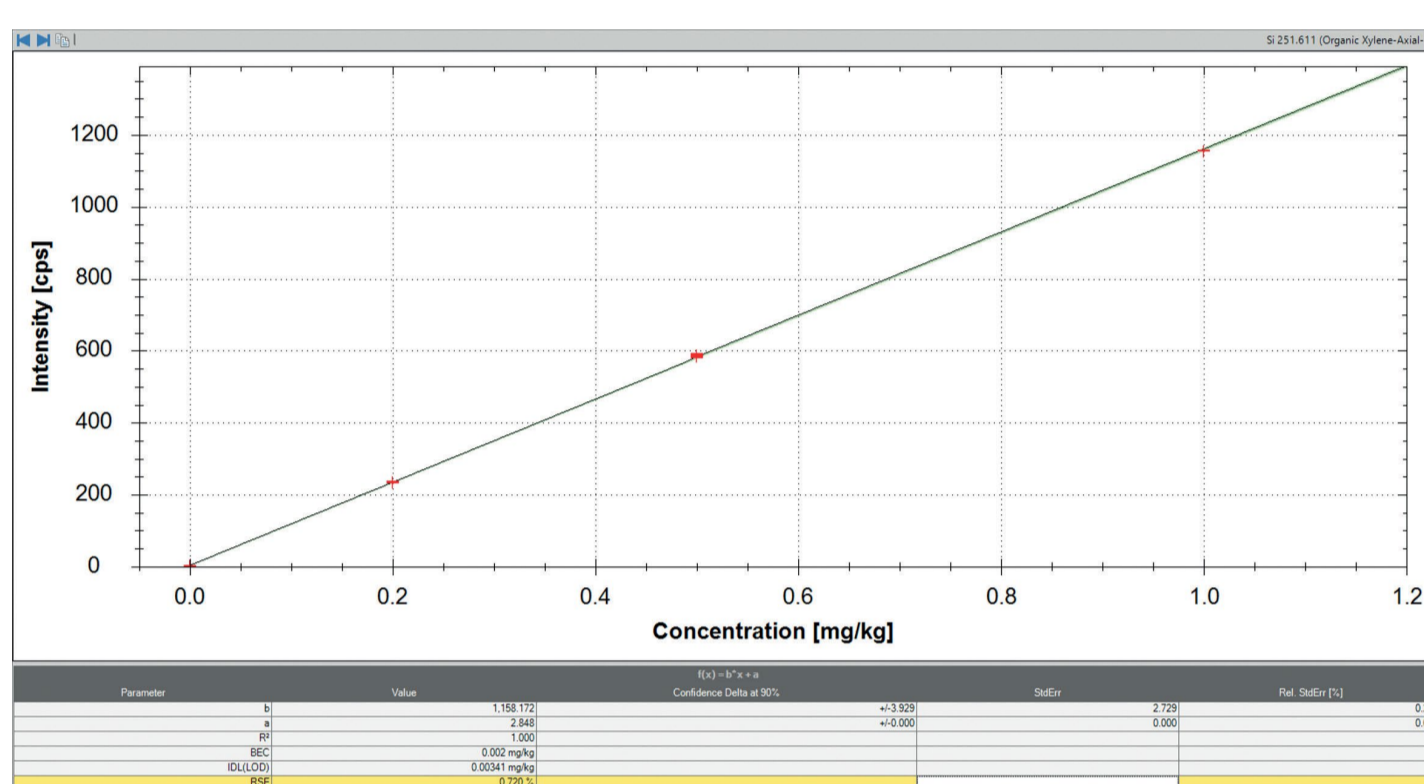
Figure 2. Calibration curve for Si 251.611 nm in Axial viewing mode assessed over a concentration range of 0.2–1 mg·kg-1

Accuracy and precision

The analytical accuracy of the method was tested by measuring spiked vegetable oil samples – very good recoveries of 90-107% were obtained for 5-fold diluted samples with RSDs below 1%. The RSD was slightly higher at 4.5% only for sodium, likely due to contamination. The results are summarized in Table 4.

Table 4. Sensitivity results, spike recovery and method detection limits (MDLs)

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

MDL = LOD x dilution factor
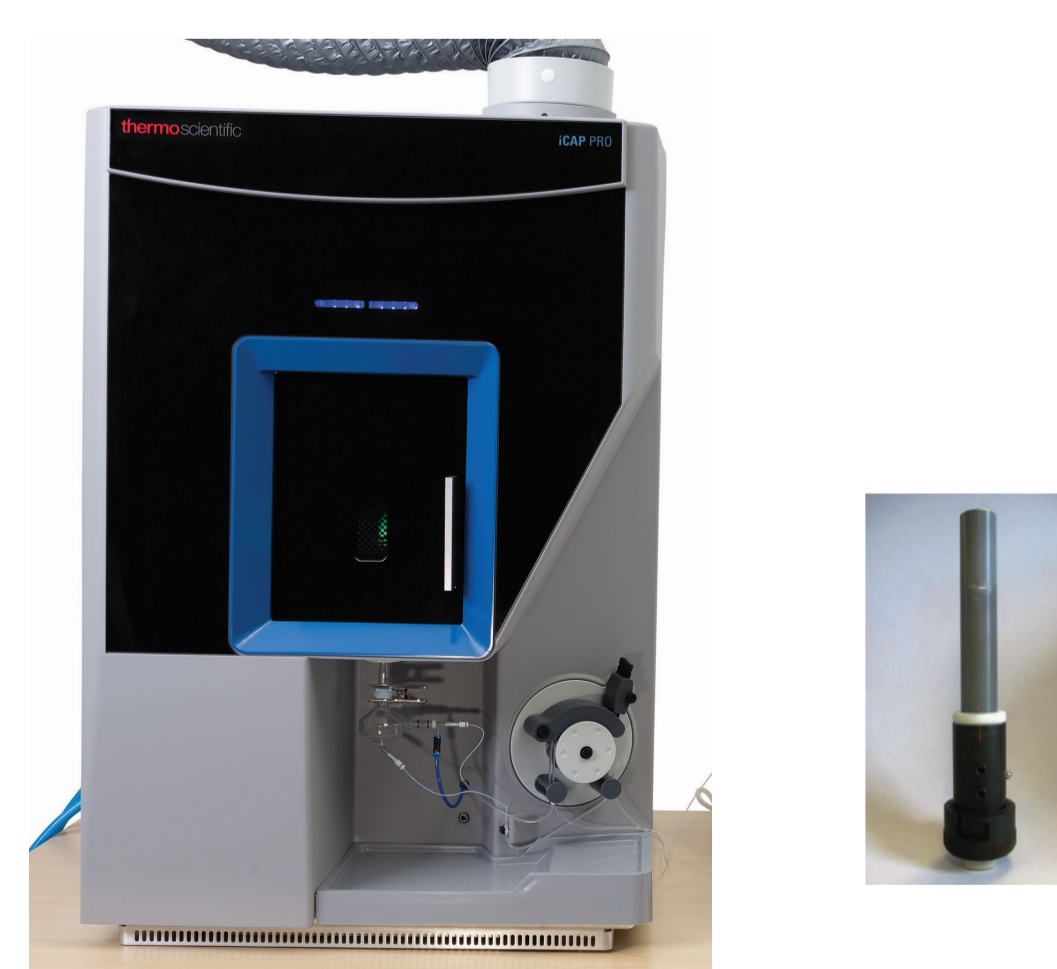
Figure 3. The iCAP PRO XP Duo ICP-OES system was used in conjunction with the ceramic D-torch

Robustness

A batch of 51 vegetable oil samples were setup for analysis within the same sequence in order to create a LabBook spanning ~ 3 hours. Batches of five unknown samples were followed by a quality control standard (continuing calibration verification, CCV) containing 1 mg·kg-1 of all target analytes and the intensities of the 1 mg·kg-1 yttrium (Y) internal standard (IS) was monitored throughout the sequence. The CCVs and IS yielded stable data in the robustness test with <±0.8% RSDs for CCV recovery (Figure 4) and 94-103% recovery of IS compared to initial blank in both axial and radial viewing modes (Figure 5).
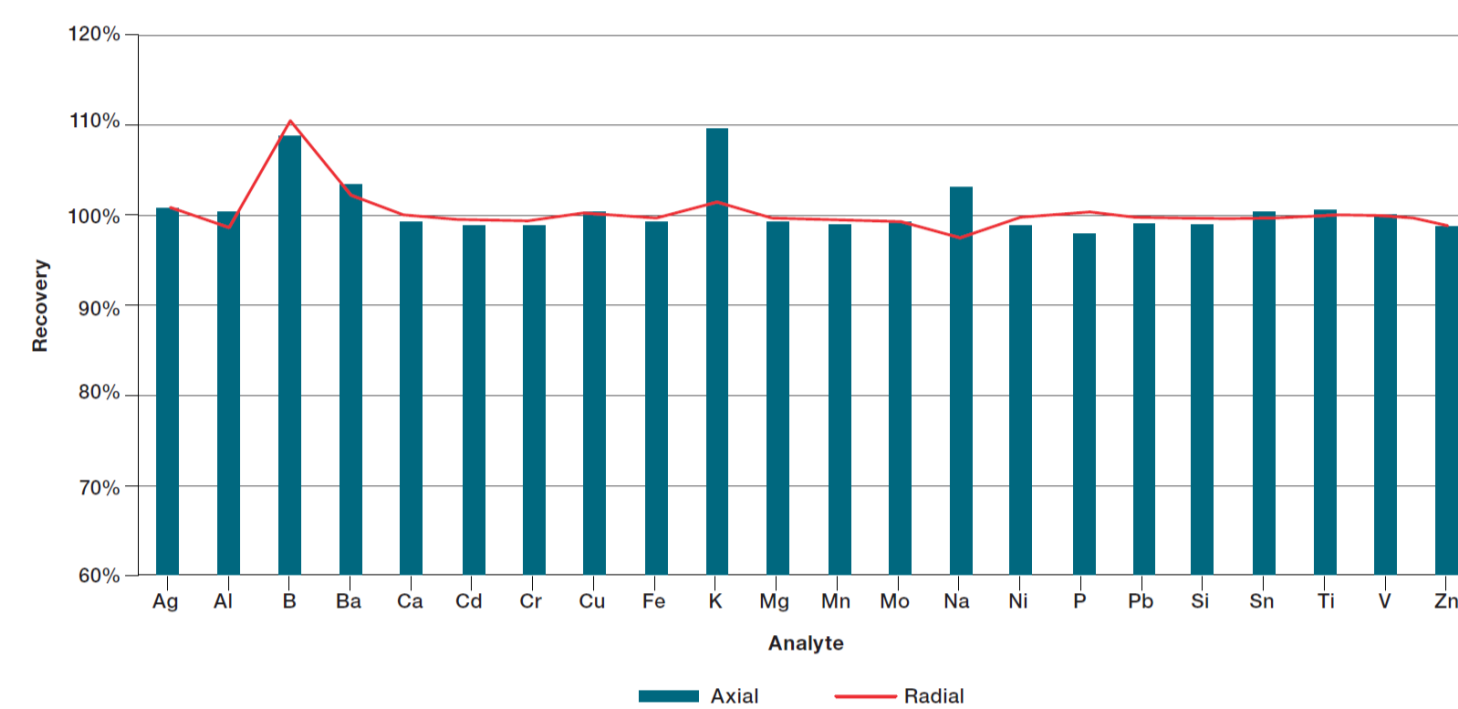
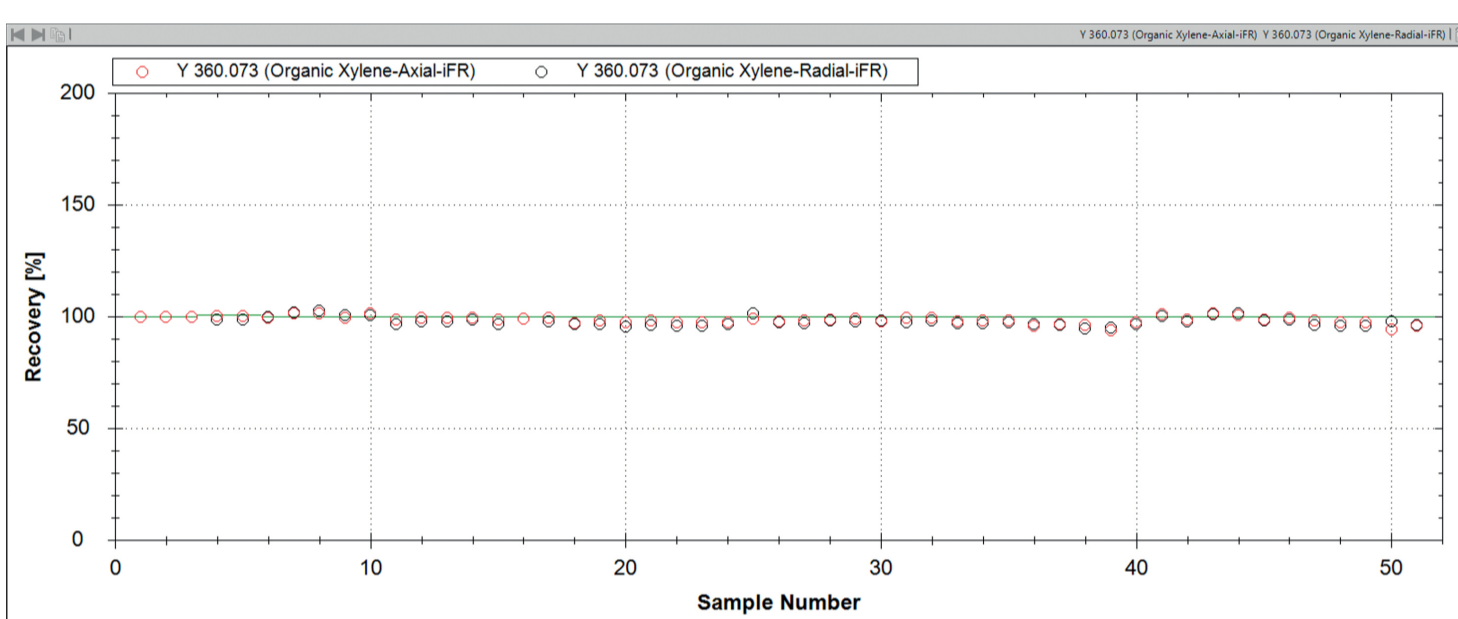**Figure 4. QC calibration verification results (n=5). CCV recovery is normalized relative to the concentration of 1 mg·kg-1.**

Figure 5. Response of the internal standard (yttrium) assessed over a period of ~3 h of uninterrupted acquisition of 51 samples

Conclusions

The iCAP PRO XP ICP-OES Duo instrument was used to analyze 22 elements, nutritional and toxic elements, in vegetable oil samples following simple 5x dilution with xylene. This fast approach provided excellent results and reliable high-quality data.

- High sensitivity was achieved for all elements including challenging ultraviolet region elements like lead, phosphorus etc. The demountable and robust ceramic D-torch enabled excellent sensitivity and stability for Si (10-fold lower background observed compared to a quartz torch).

- Excellent spike recovery results (±10%), QC results (RSD ±0.8%) and stable IS data was obtained.

- The quality of analytical data obtained suggests that the intended analysis can be performed reliably with the iCAP PRO XP ICP-OES Duo with vertical torch design offering sensitivity of axial mode and robustness of radial only instrument in single measurement.

- The Qtegra ISDS Software allows easy and flexible selection of the eUV wavelength range as well as both plasma viewing modes (Axial, Radial) making this method ideal for regular vegetable oil analysis and quality control, but also unlocks a wide range of capabilities for analytical research.

References

1. Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

2. Japan Ministry of Health, Labor and Welfare. https://www.e-healthnet.mhlw.go.jp/

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