

The Determination of Trace Elements in Edible Oils Using the Prodigy Plus ICP-OES

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Edible oils are derived from a wide variety of plants and plant seeds and are refined for global use in foods such as salad dressings, margarine, shortenings, snack foods and frying oil.

Vegetable oils have naturally occurring high contents of phosphorus (in the form of phospholipids), calcium and magnesium and contain traces of other elements like iron and copper. Significant concentrations of these substances in the final product can affect flavor, color and stability. To improve product quality, these substances are removed during the refining process.



Hydrogenation is a chemical process that changes the property of an edible oil to improve its stability and physical characteristics using a nickel catalyst. Complete removal of nickel in the final product is a necessity since it increases the rate of oxidation and causes the oil to turn rancid, resulting in a shorter shelf-life. Consequently, accurate trace metals analysis is a required quality control measure throughout the refining process.

ICP-OES's sensitive and selective methodology meets this need with the ability to determine up to 70 elements in a sample throughout the various stages of the refining process. This application note describes the analysis of edible oils using a Teledyne Leeman Lab's radial view Prodigy Plus ICP and provides the most suitable wavelengths, background correction and integration times. Results of a detection limit study are presented. The accuracy of the analytical method is validated using various oil matrices.

Instrument and Method

This study was performed using a Teledyne Leeman Labs' Prodigy Plus ICP configured for radial viewing. The conditions used in this study are given in [Table I](#) and were found to be optimal for this application. It should also be noted that even for very different oil matrices, these conditions would not be expected to change significantly.

The Prodigy Plus is a compact bench-top simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel large-format CMOS detector. At 28 x 28 mm, the active area of the detector is significantly larger than any other solid-state detector currently offered for ICP-OES. This combination allows the Prodigy Plus to achieve higher optical dispersion than other solid-state detector-based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. The detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than six orders of magnitude. The Prodigy Plus also uses a 40.68 MHz rugged, water-cooled, free-running RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

Sample Introduction

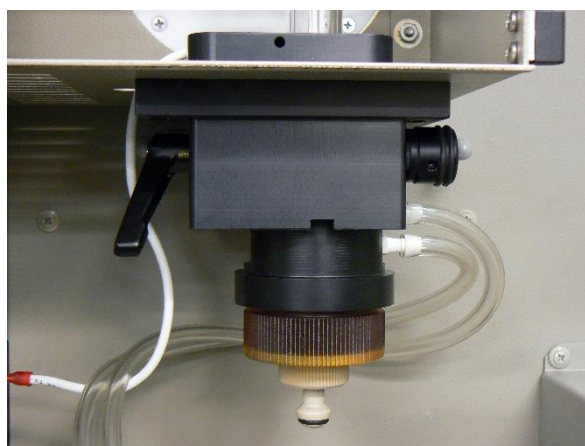
For this study, the sample introduction system consisted of:

- Cyclonic spray chamber with a center knockout tube (PN 120-00475-1)
- Rytan™ V-groove nebulizer (PN 120-00045)
- Four-channel peristaltic pump

The volume of the cyclonic spray chamber is low allowing for fast washout between samples, while its knockout tube (or baffle) efficiently reduces the amount of sample aerosol that reaches the plasma torch. The Rytan™ V-groove nebulizer is sensitive, inert, requires no adjustment and is virtually impossible to clog.

The Prodigy Plus's torch is mounted using a unique twist-n-lock cassette system, shown in [Figure 1](#). The design permits operators to remove and replace the torch to the same exact position, providing day-to-day reproducibility and simplified training. Because coolant and auxiliary gas flow connections are made automatically, potential errors are eliminated.

Figure 1 Twist-n-Lock Sample Introduction System



Operating Parameters

For all elements of interest, background correction was performed simultaneously with the peak measurement, resulting in improved detection limits. All samples were analyzed with a radially oriented instrument. The operating conditions used for all data collection are listed in [Table I](#). Optimal operating conditions were not expected to be significantly different for each oil matrix, as the viscosity of the calibration standards was closely matched to that of the samples analyzed. Consequently, one set of operating conditions was adequate for all sample analyses.

Table I Plasma Operating Conditions		
Parameter	Instrument Setting	P/N
RF Power, kW	1.2	
Coolant Gas L/min	16.0	
Auxiliary Gas L/min	1.4	
Nebulizer PSI	25	
Pump Rate RPM	20	
Torch	Quartz Demountable	318-00167-1
Injector	1.1 mm bore	318-00161-ORG2
Integration time	20 sec.	

Calibration Standards

To prevent matrix effects in the sample introduction system, the viscosities of samples and standards were matched as closely as possible, and the viscosities of all oils tested were approximately the same. Under these conditions, the use of an internal standard to correct for differences in aerosol transport efficiencies was not necessary. High-purity kerosene was used as a solvent for all samples and standards and all dilutions were performed on a weight-to-weight basis. The edible oil matrices were prepared using a dilution ratio of 1:10. The calibration standards for the detection limit and spike recovery studies were prepared by diluting VHG V23 metallo-organic standards using a dilution ratio of 1:10. Standards were prepared at 0.00, 500, 1000 and 5000 ppb levels. The 5000 ppb standard was used only for Ca, Fe, K, Mg, and Na. For matrix-matching purposes, the 0.00 ppm standard was prepared by diluting VHG® base oil 75 at a ratio of 1:10.

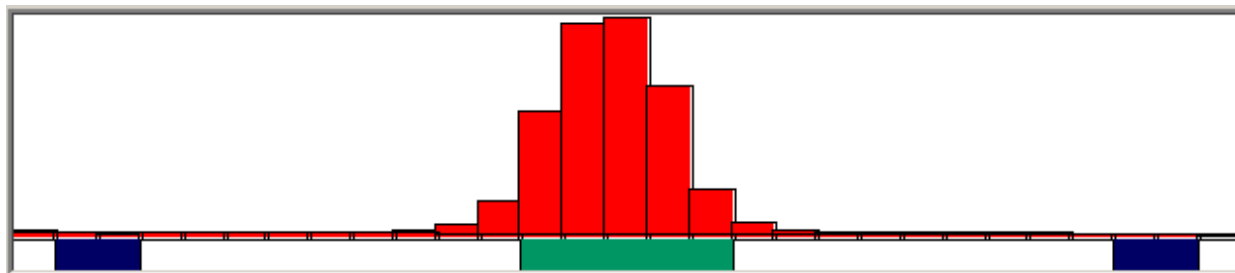
Wavelength Parameters

The Prodigy Plus ICP typically uses a 29 pixel-wide subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 57 pixels in width, if needed. The analytical peaks and background correction points are defined in each subarray with pixel position and width values. The wavelengths used in this method are outlined in [Table II](#). The default starting position and pixel width was used for all analytical peaks. For each analyte of interest, background correction was performed simultaneously with the peak measurement. In addition, all pixel data is automatically saved, allowing for future data recalculation.

Table II Wavelengths			
Element	Wavelength nm	Element	Wavelength nm
Ag	328.068	Mo	281.615
Al	308.215	Na	589.592
Ba	455.403	Ni	221.648
Ca	396.847	P	213.618
Cd	214.441	Pb	220.353
Cr	267.716	Si	251.611
Cu	324.754	Sn	189.991
Fe	259.940	Ti	334.941
K	766.491	V	309.311
Mg	279.553	Zn	202.548
Mn	257.610		

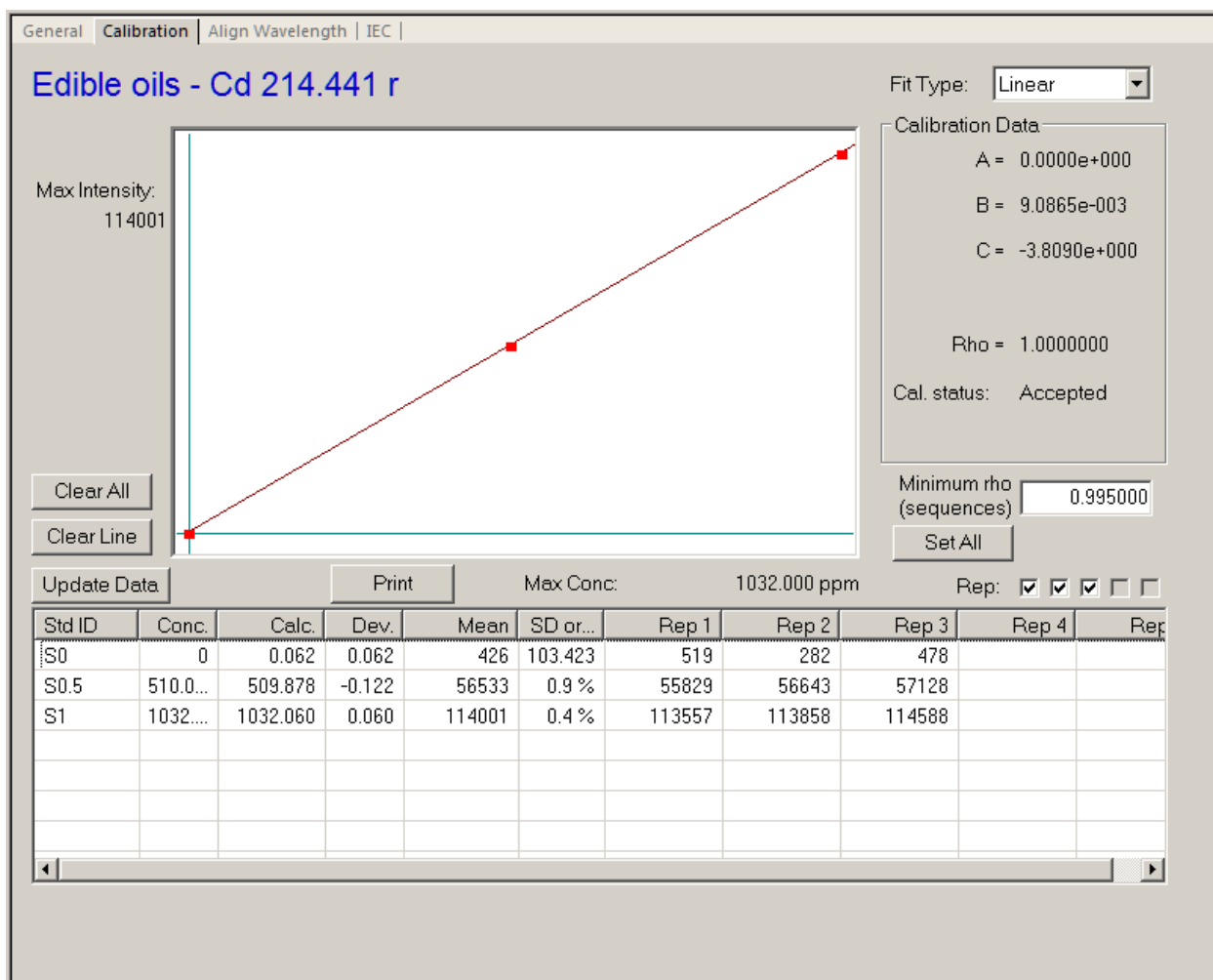
An example of the data collection that takes place in each subarray is illustrated graphically in [Figure 2](#). This figure represents the data collected for olive oil spiked with 1000 ppb multi-element standard at the Ag 328.068 nm line. The left and right background correction points are illustrated at pixel positions 2 and 27, with a width of 2. The pixels used for integrating the analytical peak are at pixel positions 13-17.

Figure 2 Sub Array data of the Ag 328.068 nm Line



An example of a typical calibration curve is illustrated in [Figure 3](#). The figure is based on calibration data for the Cd 214.441 nm line and demonstrates typical precision and linearity for the range of concentrations included in the calibration.

Figure 3 Typical Calibration Curve for Cd 214.441 nm



Results and Discussion

Samples

After igniting the plasma and allowing a 15-minute warm-up period, the instrument was calibrated using the calibration blank and standards. Following calibration, the edible oil samples were analyzed. Results for corn, soybean, vegetable, peanut, olive and canola oil samples are presented in [Table III](#), through [Table VII](#). Results for each oil sample are reported in units of parts per billion (ppb) and are corrected for the 1:10 dilution. Results are also presented for the recoveries of a 1 ppm spike, along with %RSD values for the measured spike concentrations. Elements are listed as Not Detected (ND) if the measured concentration was below the instrument's detection limits.

Table III Peanut Oil				
Element	Wavelength nm	Measured Conc. (ppb)	Recovery	RSD
Ag	328.068	25.0	101.1	0.2
Al	308.215	ND	97.6	0.4
Ba	455.403	10.7	102.0	0.6
Ca	396.847	69.7	102.7	0.6
Cd	214.441	25.5	99.5	0.6
Cr	267.716	ND	99.0	0.7
Cu	324.754	ND	100.9	0.5
Fe	259.940	ND	99.6	0.6
K	766.491	ND	103.2	0.5
Mg	279.553	40.1	102.2	0.6
Mn	257.610	17.8	103.4	0.4
Mo	281.615	ND	98.0	0.6
Na	589.592	373.2	96.7	0.5
Ni	221.648	ND	102.8	0.5
P	213.618	ND	98.1	0.4
Pb	220.353	ND	98.6	1.4
Si	251.611	ND	101.1	0.9
Sn	189.991	ND	103.1	1.1
Ti	334.941	ND	102.0	0.6
V	309.311	ND	102.7	0.5
Zn	202.548	ND	97.1	0.7

Table IV Vegetable Oil				
Element	Wavelength nm	Measured Conc. (ppb)	Recovery	RSD
Ag	328.068	37.7	97.4	1.4
Al	308.215	ND	93.3	1.2
Ba	455.403	7.5	98.4	1.0
Ca	396.847	7.6	99.2	1.0
Cd	214.441	ND	97.1	0.9
Cr	267.716	ND	96.0	0.8
Cu	324.754	ND	97.2	1.1
Fe	259.940	ND	96.3	1.3
K	766.491	ND	99.6	0.9
Mg	279.553	11.2	99.0	1.0
Mn	257.610	10.4	100.0	1.2
Mo	281.615	ND	95.1	1.1
Na	589.592	306.6	91.8	1.0
Ni	221.648	ND	100.2	1.3
P	213.618	ND	95.9	1.0
Pb	220.353	ND	96.7	2.6
Si	251.611	ND	96.2	0.6
Sn	189.991	ND	100.3	0.2
Ti	334.941	ND	98.7	1.0
V	309.311	ND	99.5	1.0
Zn	202.548	ND	94.5	1.0

Table V Canola Oil				
Element	Wavelength nm	Measured Conc. (ppb)	Recovery	RSD
Ag	328.068	42.5	103.6	1.8
Al	308.215	ND	100.8	0.9
Ba	455.403	10.9	104.8	1.2
Ca	396.847	ND	105.5	1.2
Cd	214.441	ND	102.6	0.6
Cr	267.716	ND	101.8	0.7
Cu	324.754	ND	103.5	1.2
Fe	259.940	ND	102.1	1.1
K	766.491	ND	106.9	1.5
Mg	279.553	14.7	105.0	1.0
Mn	257.610	13.1	106.0	1.0
Mo	281.615	ND	100.6	0.8
Na	589.592	345.8	99.3	1.7
Ni	221.648	ND	106.0	0.7
P	213.618	ND	101.2	0.5
Pb	220.353	ND	102.1	0.5
Si	251.611	ND	103.8	0.5
Sn	189.991	ND	108.2	0.5
Ti	334.941	ND	104.8	0.9
V	309.311	ND	105.5	1.0
Zn	202.548	ND	100.0	0.7

Table VI Corn Oil				
Element	Wavelength nm	Measured Conc. (ppb)	Recovery	RSD
Ag	328.068	72.6	99.7	1.6
Al	308.215	ND	96.7	0.5
Ba	455.403	19.7	101.2	0.8
Ca	396.847	43.8	101.7	0.7
Cd	214.441	33.3	97.9	1.0
Cr	267.716	ND	97.9	0.5
Cu	324.754	22.2	99.8	0.9
Fe	259.940	ND	98.1	1.1
K	766.491	ND	102.7	1.9
Mg	279.553	32.3	101.1	0.8
Mn	257.610	24.9	102.1	1.1
Mo	281.615	ND	96.9	0.6
Na	589.592	423.4	95.4	0.9
Ni	221.648	ND	101.8	0.6
P	213.618	ND	97.2	1.6
Pb	220.353	ND	97.8	1.4
Si	251.611	ND	100.5	0.9
Sn	189.991	ND	102.5	1.7
Ti	334.941	ND	101.1	0.6
V	309.311	ND	101.8	0.9
Zn	202.548	ND	95.6	0.8

Table VII Olive Oil				
Element	Wavelength nm	Measured Conc. (ppb)	Recovery	RSD
Ag	328.068	25.2	95.6	1.8
Al	308.215	ND	92.5	1.4
Ba	455.403	9.6	97.2	1.1
Ca	396.847	242.7	98.0	1.1
Cd	214.441	ND	95.6	0.6
Cr	267.716	ND	94.4	0.7
Cu	324.754	23.0	95.6	1.5
Fe	259.940	ND	94.8	1.2
K	766.491	253.0	98.1	1.5
Mg	279.553	76.3	97.8	1.0
Mn	257.610	13.5	98.9	1.1
Mo	281.615	ND	93.7	0.9
Na	589.592	1408.4	90.2	1.3
Ni	221.648	ND	98.1	0.8
P	213.618	ND	94.3	1.2
Pb	220.353	ND	94.6	1.2
Si	251.611	ND	96.5	0.5
Sn	189.991	ND	100.6	0.8
Ti	334.941	ND	97.2	1.0
V	309.311	ND	98.2	1.1
Zn	202.548	ND	92.8	0.8

Detection Limits

A study was performed to determine the instrument's detection limits in radial view for the elements of interest. Detection limits were calculated based on three times the standard deviation of 10 replicate measurements of the calibration blank. Results for the detection limit study are listed in [Table VIII](#). The detection limits are corrected for the typical 1:10 dilution employed for the analysis of edible oils.

Table VIII Typical Detection Limits in the Diluted Sample					
Element	Wavelength nm	DL (ppb)	Element	Wavelength nm	DL (ppb)
Ag	328.068	22	Mo	281.615	43
Al	308.215	32	Na	589.592	207
Ba	455.403	3	Ni	221.648	59
Ca	396.847	5	P	213.618	186
Cd	214.441	22	Pb	220.353	157
Cr	267.716	34	Si	251.611	106
Cu	324.754	17	Sn	189.991	287
Fe	259.940	16	Ti	334.941	5
K	766.491	99	V	309.311	6
Mg	279.553	7	Zn	202.548	37
Mn	257.610	6			

Conclusion

Edible oils are easily analyzed using the Teledyne Leeman Labs' Prodigy Plus ICP. The spike recovery results presented in this work indicate that all analytes were measured within $\pm 10\%$ of the spiked concentrations. Those results, along with their associated %RSD values, demonstrate the Prodigy Plus's ability to provide accurate and reliable results when analyzing edible oil sample matrices. Careful matrix matching of all standards and samples eliminated the need for an internal standard to correct for differences in aerosol transport efficiencies between samples.