The Determination of Trace Elements in Edible Oils using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Introduction

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

Oils contain unsaturated fatty acids and relatively high levels of phospholipids which can react with oxygen to produce unpleasant flavors and odors in the oil. The presence of trace concentrations of metals such as Ca, Cu, Fe, Mg and Ni promote oxidation and can significantly reduce shelf life. Vegetable oils are very high in phosphorus, calcium and magnesium as well as traces of iron. As the oil is refined, the levels of these metals are continuously reduced to improve the final product's flavor, color and stability.

Additionally, oils are often partially or fully hydrogenated to improve chemical stability, resistance to oxidation and increase melting point. Nickel catalyst used in the hydrogenation process must be completely removed due to its pro-oxidant qualities that reduce shelf life by increasing the rate of oxidation and turning the oil rancid. Consequently, accurate trace metals analysis is a required quality control measure throughout the refining process.

ICP-OES's sensitive and selective methodology meets this requirement 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 7 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 soybean, olive and corn oil matrices.

Instrument and Method

This study was performed using a Teledyne Leeman Lab's Prodigy7 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. However, even for very different oil matrices, these conditions would not be expected to change significantly.

The Prodigy7 is a compact bench-top simultaneous ICP-OES system featuring a 500 mm focal length Echelle optical system coupled with a mega-pixel Large Format CMOS (L-CMOS) detector. At 28 x 28 mm, the active area of the L-CMOS is significantly larger than any other solid-state detector currently offered for ICP-OES. This combination allows the Prodigy7 to achieve higher optical resolution 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. This 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 Prodigy7 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)
- Ryton™ 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 Ryton™ V-groove nebulizer is sensitive, inert, requires no adjustment and is virtually impossible to clog.

The Prodigy 7's torch is mounted using a newly designed twist-n-lock cassette system, shown in Figure 1. This design permits operators to remove and replace the torch to the exact same position, providing day-to-day reproducibility and simplified training. Designed to make automatic connections of coolant and auxiliary gas flows, potential errors are eliminated.

Figure 1   Twist-n-Lock Sample Introduction System
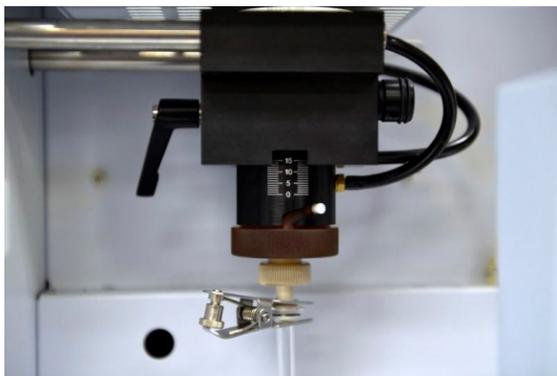
Operating Parameters

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 radial 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 able to be used for all sample analyses.

Table I Plasma Operating Conditions		
Parameter	Instrument Setting	PN
RF Power, kW	1.2	
Coolant Gas, L/min	14	
Auxiliary Gas, L/min	1.2	
Nebulizer, psi	35	
Pump Rate, rpm	20	
Torch	Quartz Demountable	318-00160-1
Injector	1.5 mm bore	318-00161-ORG1

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, 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, 1000, 2500 and 5000 ppb levels. 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 Prodigy7 ICP typically uses a 27 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 wavelength and background correction points used in this method are outlined in Table II. For elements in which background correction included more than 1 pixel on the same side, multiple values are listed to indicate the positions for all the pixels used. 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. Additionally, all pixel data was saved allowing for future data recalculation.

Table II	Wavelength and Background Correction Points		
Element	**Wavelength nm**	**Right Background Correction**	**Left Background Correction**
Ag	328.068	2 - 8	22 - 28
Al	308.215	6 - 9	23 - 28
Ba	455.403	1 - 5	26 - 29
Ca	396.847	1 - 6	24 - 29
Cd	214.441	1 - 8	23 - 29
Cr	267.716	1 - 7	25 - 29
Cu	324.754	1 - 6	24 - 28
Fe	259.94	2 - 6	24 - 29
Mg	279.553	1 - 6	23 - 29
Mn	257.61	2 - 7	23 - 29
Mo	281.615	1 - 6	27 - 29
Na	589.592	6 - 7	-
Ni	221.648	2 - 6	-
P	213.618	-	23 - 28
Pb	220.353	2 - 3	27 - 28
Si	251.611	-	24 - 28
Sn	189.991	2 - 7	23 - 28
Ti	334.941	6 - 10	27 - 28
V	309.311	6 - 10	24 - 29
Zn	202.548	1 - 8	24 - 29

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 the 1000 ppb multi-element standard (Std 2) at the Cd 214.441 nm line. In Figure 2, the left and right background correction points are illustrated at pixel positions 1 and 23, with a width of 6 and 7, respectively. The pixels used for integrating the analytical peak are at pixel positions 11-17.

Figure 2   Sub Array data of the Cd 214.441 nm Line
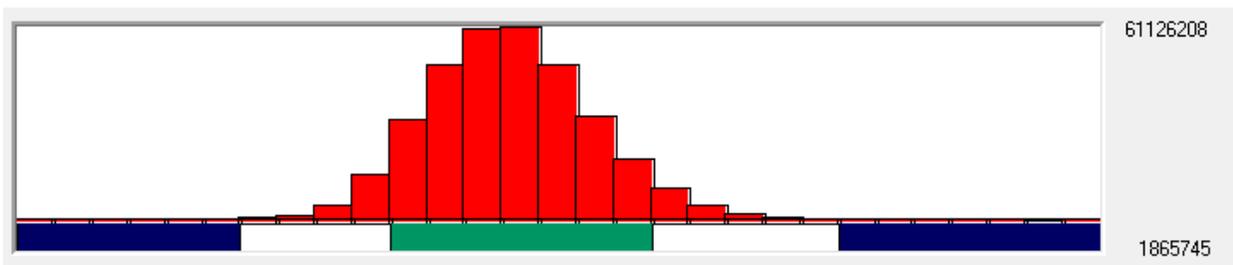
An example of a typical calibration curve is illustrated in Figure 3. The figure is based on calibration data for the Cd 214.441 nm line and demonstrates typical precision and linearity for the range of concentrations included in the calibration.

Figure 3   Typical Calibration Curve for Cd 214.441 nm
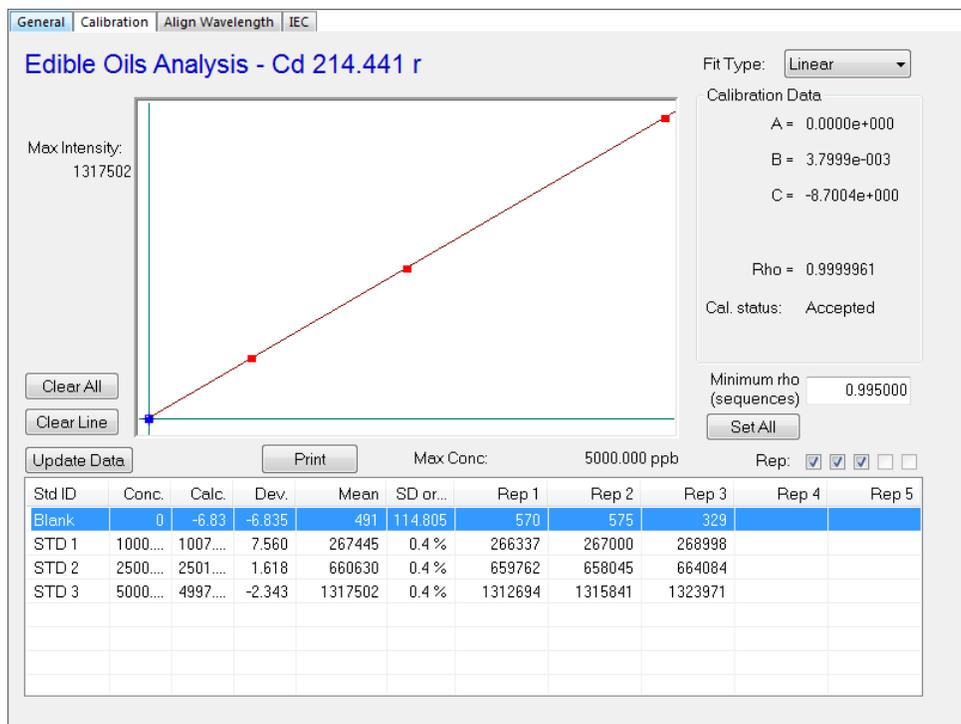
Results and Discussion

Samples

After igniting the plasma and allowing a 15 minute warm-up period, the instrument was calibrated using the calibration blank and standards listed in Table II. Following calibration, the edible oil samples were analyzed. Results for the corn, soybean, vegetable, peanut, olive and canola oil samples are presented in Table III, Table IV, Table V, Table VI, Table VII and Table VIII, respectively. 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 the 2 ppm spikes, along with %RSD values for the measured spike concentrations. Elements are listed as not detected (<DL) if the measured concentration was below the instrument's detection limits (Table IX).

Table III Corn Oil				
Element	Wavelength (nm)	Measured Conc. (ppb)	Recovery %	RSD %
Ag	328.068	51.5	98.9	0.6
Al	308.215	<DL	104.4	0.4
Ba	455.403	<DL	102.7	0.2
Ca	396.847	43.1	108.0	0.3
Cd	214.441	<DL	103.4	0.5
Cr	267.716	<DL	104.8	0.2
Cu	324.754	<DL	103.0	0.3
Fe	259.94	63.4	104.6	0.3
Mg	279.553	51.7	104.6	0.3
Mn	257.61	29.1	104.6	0.3
Mo	281.615	<DL	104.3	0.2
Ni	221.648	<DL	103.8	0.5
Na	589.592	885.4	106.7	0.8
P	213.618	<DL	102.8	0.2
Pb	220.353	<DL	104.2	0.5
Si	251.611	<DL	103.1	0.3
Sn	189.991	<DL	105.0	0.3
Ti	334.941	<DL	103.7	0.4
V	309.311	<DL	104.3	0.4
Zn	202.548	<DL	103.4	0.4

Table IV	Soybean Oil			
Element	**Wavelength (nm)**	**Measured Conc. (ppb)**	**Recovery %**	**RSD %**
Ag	328.068	68.3	96.0	1.1
Al	308.215	<DL	99.4	1.1
Ba	455.403	<DL	98.5	0.7
Ca	396.847	17.5	100.6	0.8
Cd	214.441	<DL	98.3	1.1
Cr	267.716	<DL	100.2	0.8
Cu	324.754	<DL	98.5	0.9
Fe	259.94	63.4	99.9	0.6
Mg	279.553	17.5	101.3	0.8
Mn	257.61	<DL	99.9	0.7
Mo	281.615	<DL	98.5	0.9
Ni	221.648	<DL	98.3	0.8
Na	589.592	946.1	98.6	1.0
P	213.618	<DL	98.0	0.7
Pb	220.353	<DL	99.5	0.2
Si	251.611	<DL	98.4	0.6
Sn	189.991	<DL	99.7	1.5
Ti	334.941	<DL	99.1	0.9
V	309.311	<DL	100.8	0.8
Zn	202.548	<DL	99.1	0.9

Table V Vegetable Oil				
Element	**Wavelength (nm)**	**Measured Conc. (ppb)**	**Recovery %**	**RSD %**
Ag	328.068	48.3	98.1	0.2
Al	308.215	<DL	100.8	0.2
Ba	455.403	<DL	99.2	0.2
Ca	396.847	<DL	99.7	0.4
Cd	214.441	<DL	99.4	0.2
Cr	267.716	<DL	100.6	0.1
Cu	324.754	<DL	97.2	0.1
Fe	259.94	<DL	101.0	0.2
Mg	279.553	<DL	98.7	0.4
Mn	257.61	<DL	100.0	0.1
Mo	281.615	<DL	100.2	0.4
Ni	221.648	<DL	99.0	0.3
Na	589.592	1150	97.8	0.5
P	213.618	<DL	97.9	0.2
Pb	220.353	<DL	100.9	0.4
Si	251.611	<DL	99.4	0.4
Sn	189.991	<DL	99.9	0.4
Ti	334.941	<DL	100.2	0.3
V	309.311	<DL	101.2	0.2
Zn	202.548	<DL	99.4	0.2

Table VI Peanut Oil				
Element	**Wavelength (nm)**	**Measured Conc. (ppb)**	**Recovery %**	**RSD %**
Ag	328.068	78.5	98.2	0.2
Al	308.215	<DL	101.7	0.2
Ba	455.403	<DL	100.8	0.2
Ca	396.847	100.7	101.7	0.3
Cd	214.441	<DL	100.3	0.3
Cr	267.716	<DL	101.6	0.2
Cu	324.754	<DL	100.0	0.3
Fe	259.94	<DL	101.9	0.2
Mg	279.553	<DL	100.5	0.3
Mn	257.61	<DL	100.6	0.2
Mo	281.615	<DL	100.9	0.2
Ni	221.648	<DL	99.6	0.2
Na	589.592	1580	96.9	0.4
P	213.618	<DL	100.5	0.2
Pb	220.353	<DL	102.3	0.7
Si	251.611	<DL	100.2	0.1
Sn	189.991	<DL	101.1	0.2
Ti	334.941	<DL	100.9	0.3
V	309.311	<DL	102.2	0.3
Zn	202.548	<DL	100.2	0.3

Table VII Olive Oil				
Element	**Wavelength (nm)**	**Measured Conc. (ppb)**	**Recovery %**	**RSD %**
Ag	328.068	105.4	98.8	0.7
Al	308.215	<DL	102.9	0.5
Ba	455.403	<DL	101.6	0.3
Ca	396.847	290.8	102.4	0.4
Cd	214.441	<DL	101.8	0.6
Cr	267.716	<DL	102.9	0.4
Cu	324.754	<DL	100.5	0.4
Fe	259.94	<DL	103.0	0.2
Mg	279.553	<DL	100.9	0.4
Mn	257.61	<DL	101.8	0.4
Mo	281.615	<DL	102.5	0.3
Ni	221.648	<DL	100.6	0.9
Na	589.592	2380	99.1	0.4
P	213.618	<DL	101.0	0.3
Pb	220.353	<DL	104.0	0.1
Si	251.611	100	101.7	0.4
Sn	189.991	<DL	102.9	0.6
Ti	334.941	<DL	102.2	0.2
V	309.311	<DL	103.3	0.5
Zn	202.548	<DL	101.6	0.3

Table VIII	Canola Oil			
Element	Wavelength (nm)	Measured Conc. (ppb)	Recovery %	RSD %
Ag	328.068	84.4	98.8	0.7
Al	308.215	<DL	102.9	0.5
Ba	455.403	<DL	101.6	0.3
Ca	396.847	22.8	102.4	0. 5
Cd	214.441	<DL	101.8	0.6
Cr	267.716	<DL	102.9	0.4
Cu	324.754	<DL	100.5	0.4
Fe	259.94	47.4	103.0	0.2
Mg	279.553	<DL	100.9	0.4
Mn	257.61	<DL	101.8	0.4
Mo	281.615	<DL	102.5	0.3
Ni	221.648	<DL	100.6	0.9
Na	589.592	173.2	99.1	0.4
P	213.618	<DL	101.0	0.3
Pb	220.353	<DL	104.0	0.1
Si	251.611	<DL	101.7	0.4
Sn	189.991	<DL	102.9	0.7
Ti	334.941	<DL	102.2	0.2
V	309.311	<DL	103.3	0.5
Zn	202.548	<DL	101.6	0.3

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 3 times the standard deviation of 10 replicate measurements of the calibration blank. Results for the detection limit study are listed in Table IX. The detection limits are corrected for the typical 1:10 dilution employed for the analysis of edible oils.

Table IX Typical Detection Limits (DLs) in Undiluted Sample		
Element	Wavelength (nm)	DL (ppb)
Ag	328.068	11
Al	308.215	15
Ba	455.403	3.5
Ca	396.847	1.3
Cd	214.441	9
Cr	267.716	12
Cu	324.754	18
Fe	259.940	11
Mg	279.553	0.7
Mn	257.610	3
Mo	281.615	33
Ni	221.648	25
Na	589.592	237
P	213.618	117
Pb	220.353	136
Si	251.611	48
Sn	189.991	231
Ti	334.941	5
V	309.311	4
Zn	202.548	10

Conclusion

Edible oils are easily analyzed using the Teledyne Leeman Lab's Prodigy7 ICP. The spike recovery results presented in this work indicate that all analytes were measured within ±10% of the spiked concentrations. Those results, along with their associated %RSD values, demonstrate the Prodigy7's ability to provide accurate and reliable results in edible oil sample matrices. The use of kerosene to dilute all standards and samples eliminated the need for an internal standard to correct for differences in aerosol transport efficiencies between samples.