



Determination of Trace Elements in Biodiesel Feedstocks using Inductively Coupled Plasma Optical Emission Spectrometry

Introduction

Biodiesel is a renewable fuel usually produced from virgin and waste vegetable oils. Various feedstocks such as soy, canola, and cottonseed oils can be used to manufacture biodiesel. The use of biodiesel reduces toxic emissions when compared with petroleum diesel and being a domestically produced fuel reduces dependence on foreign oil.

The primary feedstock used in many countries is soybean oil, which accounts for roughly 90% of the biodiesel produced. Due to the rising costs of soybean and other seed oils, biodiesel producers are seeking alternative, lower cost feedstocks. As a result, biological wastes such as animal fats and waste greases are gaining interest in the industry. It is estimated that the United States produces more than 11 billion pounds of animal fats and recycled cooking oils annually.

In addition to cost, these alternative feedstocks have other advantages. First, since they are recycled waste products, their use does not increase demand for raw materials, helping to address the “food or fuel” issue. Second, use of these feedstocks also allows producers to manufacture fuel from sustainable, local sources while reducing the volume of material being sent to landfills and as a result is an effective way to use the waste products of other industries.

Some alternative feedstocks used to produce biodiesel are:

- **Yellow grease**

This is usually waste cooking oil but can include other oils or fats with a free fatty acid (FFA) content of less than 15%. Though more pre-treatment is required with this feedstock when compared virgin seed oils, yellow grease is considered an economically attractive feedstock.

- **Brown Grease**

This is a mix of used oils and other materials that collect in restaurant grease traps and is removed from the wastewater stream before entering into the sewer system. This is a low quality feedstock that may have an FFA content of up to 100% requiring considerably different pre-treatment than other feedstocks. Not all biodiesel producers are capable of using brown grease.

- **DAF Oil**

This is material that is removed by the Dissolved Air Filtration (DAF) unit from a wastewater stream of a meat processing facility. As the meats are being processed, they are continuously being washed with water resulting in significant amounts of fats and protein entering the wastewater stream. The DAF unit concentrates this material, allowing it to be skimmed and removed from the wastewater discharge.

- **Animal Fat**

The most commonly used animal fats for the production of biodiesel are tallow, which is a rendered form of beef fat, and poultry fat.

To ensure quality of the final product, it is important to test the trace metal content of the raw material. In addition, it is necessary to test for various trace metals in the feedstock as their presence may have an effect during the manufacturing process. ASTM D-6751 and EN 14214 are the specifications to which the final biodiesel product must be tested.

The paper will demonstrate the use of Inductively Coupled Plasma (ICP) to determine the trace metal content of various selected biodiesel feedstocks. Data to be presented will include analysis results, recovery data, and detection limits.



Experimental

A **Teledyne Leeman Labs FuelPro Biofuels Metals Analyzer** equipped with a radial torch was used to generate the data for this application note. The FuelPro provides continuous wavelength coverage from 177-800 nm and features a 40.68 MHz free running, water-cooled RF generator, allowing it to handle even the most difficult sample matrices. FuelPro is equipped with a high sensitivity organic sample introduction system (P/N 117-00069-1) which consists of a four-channel peristaltic pump, cyclonic spray chamber, single piece quartz torch and a Rytan® V-groove nebulizer.

To prevent matrix effects in the sample introduction system, the viscosities of samples and standards were matched as closely as possible. Kerosene was used as a diluent for all samples and standards and all dilutions were performed on a weight-to-weight basis. The feedstock samples were prepared by diluting 1:10 with kerosene. A second feedstock sample was also spiked with 5 ppm of each analyte to determine % recoveries.



The calibration standards were prepared by diluting Teledyne Leeman Labs MOB® organo-metallic standards with kerosene. For matrix-matching purposes, the calibration standards were prepared by diluting 75 wt base oil in a 1:10 ratio. Standards were prepared at the 0, 2.5, 5, 10, 25 and 60 parts-per-million (ppm) level for all elements. A matrix blank for the detection limit study was prepared by diluting a high-purity base oil sample in a ratio of 1:10 with kerosene. A typical linear calibration curve is shown in Figure 1.

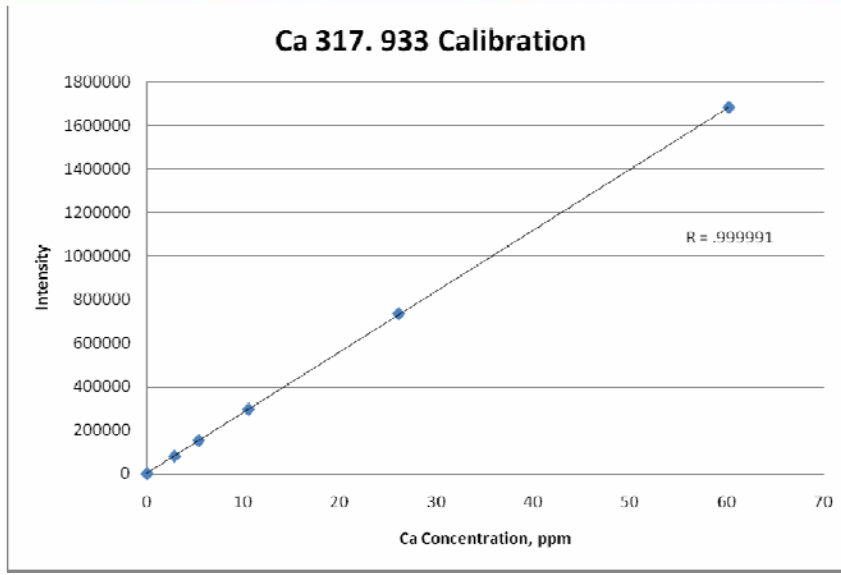


Figure 1 Calibration Curve Example

To compensate for any potential viscosity differences between samples and standards, a 5 ppm Co solution was used as an internal standard. The FuelPro’s WinICP software automatically applies any necessary corrections.

FuelPro’s operating parameters for the feedstock analysis are shown in Table 1 and were chosen for routine organic sample analysis to provide both a stable plasma and the best signal-to-background ratios. These parameters are automatically stored and are recalled whenever the method is re-opened.

Parameter	Value
RF	1.2kW
Coolant Flow	16 L/min
Auxiliary Flow	1.5 L/min
Nebulizer Pressure	50 psi
Optical Purge	0.7 mL/min
Sample Uptake Rate	0.8 L/min
Sample Uptake Tubing	Black/Black Tab P/N 309-00069-7
Internal Standard Tubing	Orange/Yellow Tab P/N 309-00069-2
Drain Tubing	Red/Red P/N 309-00069-5

Table 1 Operating Parameters

The wavelengths, background correction points and integration times used for the study are displayed in Table 2.

Element	Peak λ , nm	Peak Integration Time, sec	Background λ , nm	Background Integration Time, sec
Co	228.616	1	228.592	1
Ca	317.933	1	317.899	1
Na	589.592	5	589.555	1
K	766.490	5	766.442	1
Cu	259.940	1	324.725	1
Zn	213.856	1	213.833	1
P	213.618	1	213.641	1
Ni	231.604	1	231.583	1
Cr	267.716	1	267.74	1
Mg	285.213	1	285.188	1

Table 2 Wavelength Parameters

A typical wavelength scan is illustrated in Figure 2. During analysis, the concentration measurement is made directly in the center of the plot while the background correction measurement is made at the blue line on the left hand side.

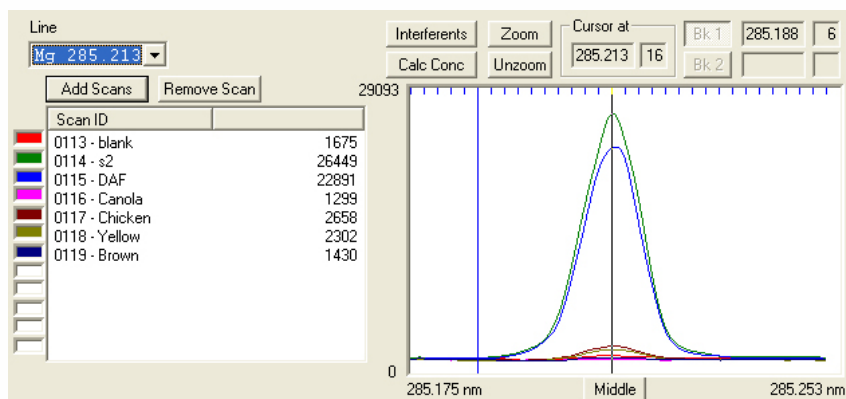


Figure 2 Wavelength Scan for Mg 285.213 nm

Results and Discussion

The results of the sample analyses and spike recoveries are presented in Tables 3 & 4. All concentrations are in parts-per-million (ppm) and are corrected to reflect the 1:10 sample dilution. The entry "ND" indicates the analyte was not detected. Spike recoveries were excellent for all of the elements in each of the feedstocks analyzed.

	DAF OIL			CANOLA	
	Concentration, ppm	% Recovery		Concentration, ppm	% Recovery
Ca	401.2	102.3		0.603	100.6
Na	8.19	98.2		1.414	100.7
K	7.93	93.7		2.059	97.6
Fe	17.12	97.4		0.104	94.6
Cu	0.869	101.9		0.118	101.5
Zn	2.40	100.5		0.099	100.6
P	223.8	102.8		0.799	97.0
Ni	0.948	96.9		0.339	95.1
Cr	0.269	100.9		ND	98.1
Mg	27.31	102.3		ND	101.9

Table 3 Analysis Results

	CHICKEN FAT		YELLOW GREASE	
	Concentration, ppm	% Recovery	Concentration, ppm	% Recovery
Ca	2.100	98.4	0.956	98.3
Na	21.59	98.4	18.09	99.5
K	32.46	93.3	7.432	91.3
Fe	0.108	93.9	0.630	96.1
Cu	0.201	102.3	0.190	99.1
Zn	0.127	99.3	0.167	96.1
P	102.1	89.8	3.685	94.7
Ni	0.305	93.3	0.220	96.9
Cr	ND	97.9	ND	98.3
Mg	0.813	100.3	0.353	100.9

Table 4 Analysis Results continued

	Brown Grease	
	Concentration, ppm	% Recovery
Ca	356.5	106.5
Na	8.195	98.1
K	7.929	93.7
Fe	17.12	97.4
Cu	0.869	101.9
Zn	2.403	100.5
P	223.9	102.8
Ni	0.949	96.9
Cr	2.69	98.5
Mg	27.32	102.3

Table 5 Analysis Results

Typical detection limits (DL) obtained in the oil matrix are shown below. The DLs were determined by taking 3 replicate measurements in blank oil and multiplying the standard deviation by three. The detection limits indicate that the FuelPro can easily measure the analyte levels required for ASTM D- 6751.

Element	DL, ppm	DL in Undiluted Samples, ppm
Ca	0.003	0.03
Na	0.019	0.19
K	0.070	0.70
Fe	0.011	0.11
Cu	0.003	0.03
Zn	0.011	0.11
P	0.023	0.23
Ni	0.006	0.06
Cr	0.011	0.11
Mg	0.009	0.09

Table 6 Detection Limits in Undiluted Feedstocks, ppm

Conclusion

Biodiesel and its feedstocks are easily analyzed using the FuelPro Biofuel Metal Analyzer. The detection limit capability of the instrument easily meets the requirements of the ASTM and EN Standards against which biodiesel must be measured.

Samples are easily prepared by dilution with a suitable solvent such as kerosene. Excellent recoveries are obtained from spiked biodiesel samples. This indicates that the method is suitable for the analysis of biodiesel feedstocks and that matrix interferences are not a problem