APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Analysis of Wear Metals and Additive Package Elements in New and Used Oil Using the Optima 8300 ICP-OES with Flat Plate Plasma Technology

Introduction

The analysis of new and used oil for concentration trends of wear metals and for formulation or depletion of additive package metals has been around for over 30 years. Wear metals such as copper (Cu) and iron (Fe) may indicate wear in an engine or any oil-wetted compartment. Boron (B), silicon (Si) or sodium (Na) may indicate contamination from dirt or antifreeze leading to a failure. Additive elements such as calcium (Ca), phosphorus (P) and zinc (Zn) are analyzed for depletion which contributes to wear since these elements contribute to certain key lubrication characteristics. A sound maintenance program, which routinely measures metals in the lubricating oils, not only reduces the expense of routinely dismantling the components for visual inspection, but can indicate unexpected wear before component failure.

Atomic absorption spectrometers (AAS) were first used for these applications in the early-to-mid 1960s. As the number of elements and samples grew over the years, inductively coupled plasma-optical emission spectrometers (ICP-OES) were used for oil analysis. Today, many oil analysis labs will handle between 500 to 2000 samples per day and analyze from 15 to 24 elements per sample.

Many improvements to ICP technology have taken place over the years with the most recent being the replacement of the helical load coil used to generate the plasma. The Optima™ 8x00 ICP-OES series (Figure 1 – Page 2) utilizes the new Flat Plate™ plasma technology that replaces the traditional helical coil design used since the inception of the inductively coupled plasma. The Flat Plate plasma technology utilizes two flat induction plates

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(Figure 2) to produce a plasma that is compact, dense and robust. This plasma utilizes about half the argon required by previous helical coil designs while still delivering exceptional analytical performance. The Flat Plate system produces a flat-bottom plasma that minimizes the escape of sample and vapors around the outside of the plasma, making organic sample analysis easier. Plasma argon flow has been reduced to 10 L/min versus the typical 15-18 L/min used by helical systems for this application which helps to reduce the cost of analysis.

Figure 1. PerkinElmer Optima 8300 ICP-OES spectrometer.

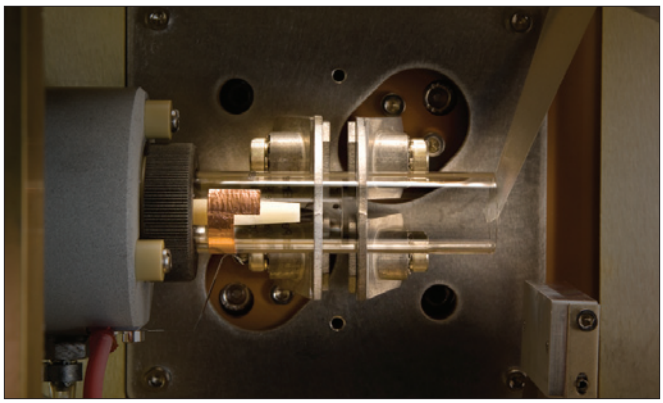

Figure 2. Torch-box of an Optima 8300 spectrometer showing the revolutionary Flat Plate plasma technology.

Experimental Conditions

Instrumentation

Data were collected using the PerkinElmer® Optima 8300 ICP-OES with a CETAC® ASX-1400 stirring autosampler (CETAC Technologies®, Omaha, NE). The standard sample introduction system is as follows:

- A low-flow GemCone™ nebulizer (Part No. N0770358)
- A 4 mm baffled cyclonic spray chamber (Part No. N0776090)
- A 1.2 mm i.d. quartz injector (Part No. N0781019)
- A screened autosampler probe (Part No. N0771529)

Plasma parameters for the analysis of wear metals and additive package elements in new and used oil using the Optima 8300 ICP-OES are listed in Table 1. The analytical wavelength for the elements analyzed are listed in Table 2. Several important parameters from the WinLab32™ software's oil method conditions are described in Table 3 (Page 3).

Table 1. **Plasma parameters for all analytes using the Optima 8300 ICP-OES.**

Parameter	Value
Source Delay (sec)	15
Plasma Aerosol Type	Wet
Nebulizer Start-up	Instant
Plasma Gas (L/min)	10
Auxillary Gas (L/min)	0.6
Nebulizer Gas (L/min)	0.35
Power (W)	1500
Viewing Distance (mm)	15.0
Viewing Mode	Radial

Table 2. **Analytical wavelengths used for detection of wear metals in oil using ICP-OES.**

Analyte	Wavelength
Ag	328.066
Al	394.408
B	249.673
Ca	315.890
Co (Int. Std.)	228.613
Cr	205.559
Cu	324.757
Fe	259.940
K	766.494
Mg	279.076
Mn	257.613
Mo	203.843
Na	588.995
Ni	231.604
P	214.915
Pb	220.351
Si	288.161
Sn	189.926
Ti	334.943
V	292.397
Zn	213.854

Table 3. **WinLab32 for ICP method parameters for the analysis of wear metals and additive package elements in oil.**

Parameter	Value
Read Delay Time (sec)	14
Replicates	2
Read Time (sec)	Automatic – Min: 0.100, Max: 2.000
Sample Flow Rate (mL/min)	4.00
Sample Flush Time (sec)	5
Sample Flush Rate (mL/min)	6.00
Wash Frequency	Every sample + extra time if limit exceeded
Wash Rate (mL/min)	5.00
Wash Time (sec)	2
Additional Wash Time (sec)	30
Peak Algorithm	Peak area (3-point)
Background Correction	2-point
Internal Standard	Co
Calibration Equation	Linear through zero
Sample Units	ppm
Quality Control Limits (%)	±10
Quality Control Fail Actions	Recalibrate, re-analyze check standard, re-analyze affected samples.

Reagents

All solutions were prepared with a CETAC® APS-1650 Automated Prep Station. Calibration standards were made using three V23 (VHG Labs®) blended standards at 500, 100, and 50 ppm (Part Nos. 500: N0776106; 100: N0776105; 50: N0776104). The V23 standards contain 23 elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Ti, V, and Zn) in 75 centistoke (cSt) hydrocarbon oil. A higher-concentration calibration standard for the additive elements was prepared using Metals Additives Standard 4 (VHG Labs) which contains Ca at 5000 µg/g plus Mg, P and Zn at 1600 µg/g (Part No. N9308259). The solvent for all cases was V-Solv™ (Part No. N9308265). The solvent for all dilutions was a solution of 2.5 grams of a 6% cobalt standard (in mineral spirits) (Part No. N0776107) added to one gallon of V-Solv™.

Sample and Standard Preparation

All samples and standards were diluted 1:10 with V-Solv™ (containing cobalt) on a CETAC® APS-1650 Automated Prep Station (Figure 3) (Part No. N0777177). The prep station picks up the oil from standard 2-4 oz bottles or 3 mL sample cups, dispenses the oil into an autosampler tube, adds solvent and mixes the sample directly in the autosampler rack. The sample preparation is done on a volume-to-volume basis.

Forty-five sample bottles, or 90 samples poured into small sample cups for dilution, can be prepared in a batch which requires approximately 35 seconds preparation time per sample. All sample information is transferred directly from the APS-1650 software into the WinLab32 software, eliminating the need to enter the data twice. Only 5 mL of diluted solution is required for the analysis. This volume allows for a sample to be analyzed twice in case of a QC failure. Cobalt is used during the analysis as an internal standard to overcome the matrix suppression caused by different oil viscosities. The cobalt can be added to the solvent diluent prior to sample dilution, thus eliminating the need to add the internal standard to each individual sample or through an online addition tubing. Since the additive elements are organic-metallic and soluble in the oil, the use of an internal standard provides a more accurate result. The wear-metal elements are suspended in the oil matrix and the results compare favorably to other analysis techniques.

Figure 3. CETAC® APS-1650 Automated Prep Station for use with an Optima 8300 ICP-OES.

Another sample and standard dilution option would be the PerkinElmer OilPrep™ 8 Oil Diluter (Figure 4, Page 4) (Part No. L1610000). To meet the need for increased throughput in wear-metal analysis programs, the OilPrep 8 Oil Diluter is equipped with ultrasonic liquid-level detection (patent pending) and an 8-tip Varispan™ pipetting arm option for rapid "on-the-fly" reformatting and diluting of samples in various sized vessels. The system utilizes multiple syringes along with disposable tips to increase sample throughput while eleminating carryover between samples and solvent waste (no rinsing is required). The sample preparation is done on a volume-to-volume basis. Ninety-six sample bottles, or any larger numbers of smaller sample containers, can be prepared at a time. Throughput can be as high as 300 samples per hour. All sample information is transferred directly from WinPREP® software into the WinLab32 software, eliminating the need to enter the data twice.

Figure 4. PerkinElmer OilPrep 8 Oil Diluter pipettes 8 samples simultaneously.

Increased ICP Sample Throughput

ICP sample analysis time can be greatly reduced by adding a sampling valve to the ICP such as the CETAC® ASXpress™. A standard analysis system relies upon a single peristaltic pump to both deliver samples to the nebulizer and rinse the sample flow path between sample deliveries. The ASXpress™ system utilizes a high-speed vacuum pump in addition to the ICP-OES peristaltic pump (Figure 5). The 6-port valve allows the use of both pumps simultaneously, reducing total sample analysis time significantly. The use of the valve effectively divides each analysis into two stages. First, while the valve is in the load position, the vacuum pump rapidly fills the sample loop, while the ICP-OES peristaltic pump simultaneously transports carrier solution, keeping the plasma stable. In the second position, the loaded sample is pushed into the nebulizer for analysis via the carrier solution flowing through the ICP-OES peristaltic pump. At the same time, the autosampler probe is moved to the rinse station and the uptake flow path is flushed with rinse solution via the vacuum pump. Improvements from this approach are:

- Analysis time per sample can be as short as 20 seconds (2 replicates per sample) without any degradation in the analysis precision or long-term stability.
- Less carbon build-up on the torch and/or the injector.
- Stability is increased for a longer period of time, requiring less recalibration and improving QC.

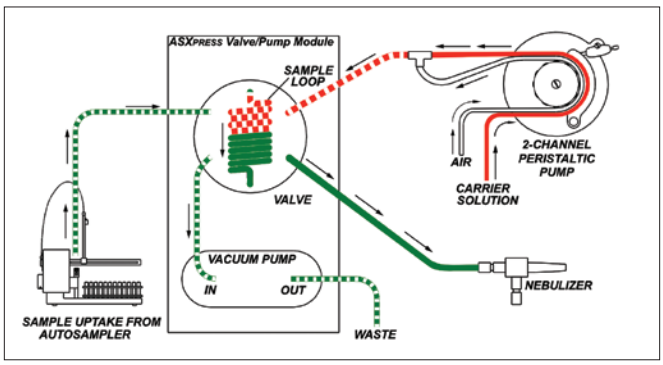

Figure 5. Schematic of the CETAC® ASXpress™ Rapid Sample Introduction System.

Results and discussion

Below are the mean results obtained for the analysis of a used oil sample utilizing the Optima 8300 without the ASXpress™ (Table 4). Analysis time per sample was 45 seconds, which includes washing between samples and two replicate readings per sample. Two check standards for low (wear metal – 50 mg/L) (Table 5, Page 5) and high concentrations (additive elements – 1600 mg/L), were analyzed every 20 to 40 samples with upper and lower limits set at ±10%. With the stability of the Optima 8300 system, the check standards rarely failed in an 8-10 hour period. If a check standard should fail, the action selected in the software is to recalibrate, rerun the check standard to verify it is within limits, and then rerun all samples since the last acceptable check standard. The % RSDs were as expected – low when analytes were present at typical concentration levels of > 5 ppm and higher when very little analyte was present. Similar results would be seen using the ASXpress™ with sample times of 24 seconds per sample.

Table 4. **Example of a mean result for the analysis of a used oil sample using the Optima 8300 ICP-OES (n=2).**

Analyte	Conc. (ppm)	Std. Dev. (ppm)	% RSD
Ag	ND	---	---
Al	6	0.10	1.6
B	51	0.04	0.09
Ca	828	10	1.2
Cr	3	0.03	1.2
Cu	23	0.29	1.2
Fe	481	5.1	1.1
K	6	0.58	9.6
Mg	18	0.06	0.3
Mn	12	0.04	0.31
Mo	3	0.38	15
Na	5	0.08	1.5
Ni	2	0.23	13
P	947	0.13	0.01
Pb	2	0.28	14
Si	24	0.45	1.9
Sn	1	0.18	16
Ti	ND	---	---
V	ND	---	---
Zn	503	5.5	1.1
Co (Int. Std.)	92%	0.70	0.76

Table 5. **Example of a single 50 ppm QC sample.**

Analyte	% Recovery	Std. Dev. (ppm)	% RSD
Ag	100	0.04	0.09
Al	106	0.59	1.1
B	99.3	0.05	0.09
Cr	103	0.29	0.56
Cu	99.5	0.09	0.18
Fe	102	0.05	0.10
K	101	0.20	0.39
Mn	103	1.1	2.2
Mo	99.2	0.28	0.56
Na	103	1.0	2.1
Ni	101	0.61	1.2
Pb	103	2.0	3.9
Si	103	1.2	2.3
Sn	103	0.68	1.3
Ti	101	1.1	2.3
V	103	0.04	0.07
Co (Int. Std.)	100	0.54	0.54

Ca, Mg, P and Zn were not reported as QC analytes.

Conclusion

The PerkinElmer Optima 8300 ICP-OES handles the diluted oil matrix very easily and increases sample throughput over previous Optima models to 45 seconds per sample with little carryover between samples. The Optima 8300 is the ideal ICP spectrophotometer for oil laboratories with moderate workloads. For laboratories with a heavy workload, an Optima 8300 combined with a CETAC® APS-1650 Automated Prep Station or a PerkinElmer OilPrep 8 Oil Diluter and CETAC® ASXpress™ Rapid Sample Introduction System is suggested.

The Optima 8000 ICP-OES, also equipped with Flat Plate plasma technology, may also be used for this analysis.

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