Analysis of wear metals and contaminants in engine oils using the 4100 MP-AES

Application note

Energy and fuels

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Introduction

The regular tracking of the metals present in oils used to lubricate machinery is a vital preventive maintenance task used to gauge the condition of the lubricant and machine over time. Analysts are particularly interested in the elements found in engines, such as Cu, Fe and Al, which are present in the oil as a result of wear and tear, and elements like Na and Si, which are present as a result of contamination from water or road dust. The trend analysis of these metals is performed on the oils so that any action required to keep the engine in service can be taken and costly repairs and downtime can be avoided.

With engines and machinery being central to most transport and manufacturing industries, many laboratories are required to analyze a high volume and variety of oil samples a day, for multiple elements. While flame atomic absorption spectrometry (FAAS) has been used extensively to study trace wear metals in used oils, the sheer number of samples has forced many laboratories to consider a faster, multi-element technique that is capable of high sample throughput.

This can now be effectively achieved using fast sequential atomic emission spectroscopy in the form of the Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. Both aqueous and organic samples can be introduced into the MP-AES, which has good tolerance to the organic solvent load.

Experimental

Instrumentation

An Agilent 4100 MP-AES was used with an External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions. The instrument was set up with the Organics kit comprising the EGCM, the inert OneNeb nebulizer [1] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers superior performance for this application over other comparable nebulizers as it offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery.

The instrument is controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b. Viewing position and nebulizer pressure settings were optimized using the auto-optimization routines in MP Expert. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required.

Samples and sample preparation

Standards were prepared at concentrations of 5 ppm, 10 ppm, 25 ppm and 50 ppm from a 500 ppm oil-based metal calibration standard S21+K (Conostan). Shellsol 2046 (Shell) was used as the diluent. All standards were matrix-matched with 10% Blank Oil (Conostan).

NIST SRM 1085b Wear Metals in Lubricating Oil was prepared by performing a 1:10 dilution in Shellsol.

A sample consisting of a mix of used gear oils was diluted 1:10 with Shellsol and spiked with S21+K, giving a final spike concentration of 10.2 ppm.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Rinse time	45 s
Fast pump (80 rpm) during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte nebulizer pressures and calibration cuves

Element & wavelength (nm)	Nebulizer pressure (kPa)	Calibration curve
Cd 228.802	140	Rational
Mn 259.372	120	Rational
Fe 259.940	100	Rational
Cr 276.653	140	Rational
Pb 283.305	220	Rational
Sn 303.411	240	Rational
Ni 305.081	180	Linear
V 310.229	220	Rational
Mo 319.398	240	Rational
Ti 323.452	220	Rational
Cu 327.395	200	Linear
Ag 328.068	200	Linear
Al 396.152	240	Rational
Na 589.592	240	Linear
Si 251.611	140	Linear

Results and discussion

Analysis of standard reference materials

To test the validity of the method, NIST SRM 1085b was analyzed. The results presented in Table 2 show excellent agreement (accuracy) between the MP-AES measured results and the certified values.

Table 2. Measured results versus certified values

Element & wavelength (nm)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Fe 259.940	314.7 ± 0.3	301.2 ± 5.0	104
Mn 259.372	289.9 ± 0.2	300.7 ± 2.0	96
Cd 226.502	290.9 ± 2.9	302.9 ± 5.1	96
Cr 276.653	305.2 ± 0.1	302.9 ± 3.9	101
Si 251.611	295.7 ± 1.9	300.2 ± 5.0	99
Ni 305.081	291.6 ± 0.1	295.9 ± 7.4	99
Cu 327.395	300.9 ± 0.1	295.6 ± 8.5	102
Ag 328.068	308 ± 0.2	304.6 ± 8.9	101
Pb 283.305	296.1 ± 0.1	297.7 ± 6.8	99
V 310.229	287.6 ± 0.1	297.8 ± 4.6	97
Ti 323.452	293.9 ± 0.1	301.1 ± 2.9	98
Sn 303.411	295.3 ± 0.3	299.4 ± 4.8	99
Mo 319.398	296.9 ± 0.1	300.6 ± 3.2	99
Al 396.152	291.7 ± 0.2	300.4 ± 9.3	97
Na 589.592	297.4 ± 0.1	305.2 ± 7.0	97

Spike recoveries

The recoveries obtained for the spiked mixed gear oil sample are presented in Table 3. Excellent recoveries were obtained for all elements analyzed, demonstrating the validity of the analytical method. The signal graph and calibration curve for Cu are shown in Figures 1 and 2 respectively.

Table 3. Accurate recovery for all analytes of 10 ppm spikes in a mixed gear oils sample

Element	Wavelength (nm)	Unspiked gear oil (ppm)	Spiked gear oil (ppm)	Spike recovery (%)
Ag	328.068 nm	0.27	11.01	105
Al	396.152 nm	0.32	10.31	98
Cd	228.802 nm	0.14	9.85	95
Cr	276.653 nm	0.25	9.92	95
Cu	327.395 nm	2.68	13.14	103
Fe	259.940 nm	10.41	20.09	95
Mn	259.372 nm	0.80	11.54	105
Mo	319.398 nm	9.02	19.34	101
Na	589.592 nm	0.46	10.70	100
Ni	305.081 nm	0.07	10.13	99
Pb	283.305 nm	0.25	11.36	109
Si	251.611 nm	2.23	11.60	92
Sn	303.411 nm	0.16	10.62	103
Ti	323.452 nm	0.01	10.87	106
V	310.229 nm	0.15	10.71	104

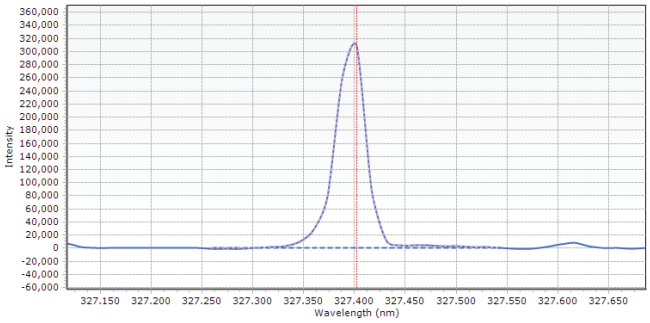

Figure 1. The signal from Cu 327.395 nm at 5 ppm shows the excellent sensitivity of the Agilent 4100 MP-AES

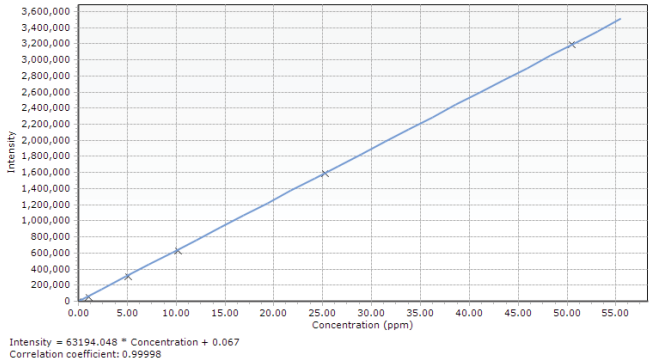

Figure 2. The calibration curve for Cu 327.395 nm up to 50 ppm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99998

Using the Agilent SPS 3 Sample Preparation System, the sample throughput time for the analysis was under 5 minutes per sample, or about 13 samples per hour. With the ability to run unattended, the 4100 MP-AES is capable of greater sample throughput than FAAS.

Long-term stability

Long-term stability of the MP-AES was investigated by continuously aspirating a 10 ppm S21+K solution over an 8 hour period. The resulting stability plot is shown in Figure 3, and the %RSDs for each element are listed in Table 4.

The sample handling capability of the vertically-oriented plasma in the 4100 MP-AES, combined with the air injection from the EGCM and the solids handling of the inert OneNeb nebulizer [1] means that excellent long-term stability (< 1% RSD) can be achieved, even when analyzing challenging organic samples.

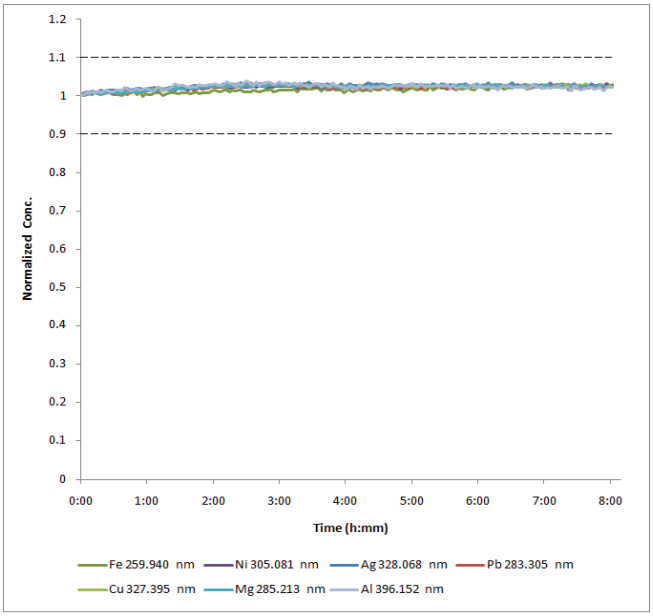

Figure 3. Normalized stability plot for 10 ppm S21+K solution run repeatedly over an 8 hour period

Table 4. %RSDs for each element spiked at 10 ppm level over an 8 hour sampling period

Element	Wavelength (nm)	%RSD
Fe	259.940	0.7
Ni	305.081	0.5
Ag	328.068	0.5
Pb	283.305	0.6
Cu	327.395	0.6
Al	396.152	0.6

Conclusions

The Agilent 4100 MP-AES equipped with a OneNeb nebulizer and fitted with the EGCM is an ideal solution for the routine multi-element analysis of wear metals in oils. Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent recoveries were achieved for SRM samples and on spiked solutions at the 10 ppm level. Excellent long-term stability was also achieved.

Reference

1. J. Moffett and G. Russell, "Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer", Agilent Application Note 5990-8340EN

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