Analysis Of Wear Metals In Lubricating Oils By Microwave Plasma - Atomic Emission Spectrometry

Philip Lowenstern, Elizabeth Reisman and Craig Taylor, Agilent Technologies, Melbourne, Australia

PWC 2012
Poster #THP03

Agilent Technologies

Introduction

The regular tracking of wear metals and trace metal contaminants present in oils used to lubricate machinery is a vital, cost-effective preventive maintenance task. Routine monitoring is vital to gauge the condition of the lubricant and machine over time, and to prevent costly repairs and unscheduled downtime due to premature component failure. 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. With engines and machinery being central to most transport and manufacturing industries, many laboratories are required to analyze multiple elements in a high volume and wide variety of oil samples every day. While flame atomic absorption spectrometry (FAAS) has been used extensively to monitor trace wear metals in used oils, the high sample workload has forced many laboratories to use alternative multi-element analysis techniques that are capable of high sample throughput. Microwave Plasma Atomic Emission Spectrometer (MP-AES) provides an ideal, low cost solution for fast, multi-element analysis of wear metals with excellent long term stability, reduced running costs and improved laboratory safety.

This paper describes the analysis of wear metal samples using the Agilent 4100 MP-AES equipped with a OneNeb nebulizer and fitted with the EGCM. 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 Standard Reference Materials and on spiked solutions at the 10 ppm level. Excellent long-term stability was also achieved. This provides an ideal solution for the routine multi-element analysis of wear metals in oils.

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. This technique produces linear dynamic range, detection limits and analysis speed superior to conventional flame AAS. Based on an atomic emission technique, this elemental analysis technique also produces greater sensitivity than flame AAS. In addition, it eliminates the need to use hollow cathode lamps. This innovative elemental analysis technique also eliminates the need for argon or indeed, any bottled gas. It operates from a compressed air supply, using the Agilent 4107 Nitrogen Generator, producing a significant reduction in operating costs and reduced infrastructure costs. As MP-AES relies on the generation of a microwave plasma using nitrogen, no flammable gases such as acetylene are required. This reduces running costs, improves lab safety and alleviates the difficulty and costs in sourcing gases such as acetylene, especially in remote locations.

Experimental

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 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.

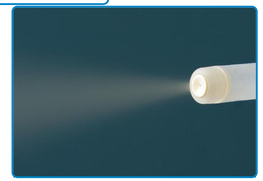
Samples and sample preparation

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 1. 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 sec
Number of replicates	3
Stabilization time	15 sec
Fast pump during sample uptake (80 rpm)	On
Background correction	Auto
Pump Speed	5 rpm



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 4100 MP-AES measured results and the certified values.

Table 2. Measured results vs certified values

Element	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	318.3 ± 0.2	302.9 ± 5.1	105%
Cr 276.653	305.2 ± 0.1	302.9 ± 3.9	101%
Si 288.158	316.7 ± 0.2	300.2 ± 5.0	105%
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	282.7 ± 0.2	300.4 ± 9.3	94%
Mn 403.076	286.3 ± 0.2	300.7 ± 2.0	95%
Cr 425.433	304.2 ± 0.3	302.9 ± 3.9	100%
Na 589.592	275 ± 0.1	305.2 ± 7.0	90%
Ba 614.171	281.2 ± 0.1	300.1 ± 2.4	94%

Table 3. Accurate spike recoveries

	Wavelength (nm)	Mixed Gear Oil (mg/kg)	Mixed Gear Oil with Spike (mg/kg)	Recovery %
Ag	328.068	0.27	11.01	105%
Al	396.152	0.32	10.31	98%
Cd	228.802	0.14	9.85	95%
Cr	276.653	0.25	9.92	95%
Cu	327.395	2.68	13.14	103%
Fe	259.940	10.41	20.09	95%
K	766.491	0.15	11.18	108%
Mg	285.213	15.97	27.16	110%
Mn	259.372	0.80	11.54	105%
Mo	319.398	9.02	19.34	101%
Na	589.592	0.46	10.70	100%
Ni	305.081	0.07	10.13	99%
Pb	283.305	0.25	11.36	109%
Si	251.611	2.23	11.60	92%
Sn	303.411	0.16	10.62	103%
Ti	323.452	0.01	10.87	106%
V	310.229	0.15	10.71	104%

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.

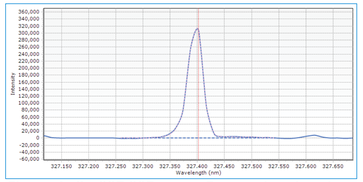


Figure 1. Cu 327.395 nm at 5 ppm showing the excellent sensitivity of the 4100 MP-AES

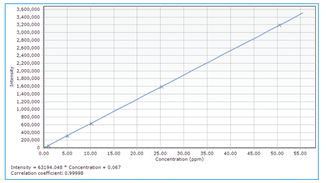


Figure 2. The calibration curve for Cu 327.395 nm up to 50 ppm shows excellent linearity

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 flame AA.

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.