Measurement of additives in lubricating oils using the Agilent 4100 MP-AES

Application note

Energy and fuels

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Introduction

The regular tracking of the additives 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. Several compounds such as Zn, P, Ca, Ba and Mg are typically added to lubricating oils. These metal-containing additives act as detergents, oxidation and corrosion inhibitors, dispersants, anti-wear agents, viscosity index improvers, emulsifiers and anti-foaming agents etc.

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 per day, for multiple elements. While flame atomic absorption spectrometry (FAAS) has been used extensively to study additives used in 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 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 with a good tolerance to organic solvent load.

Experimental

Instrumentation

An Agilent 4100 MP-AES was used with an External Gas Control Module (EGCM) for 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.

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 of mixed gear oils were diluted 1:100 with Shellsol and a spiked with S21+K giving a final spike concentration of 10.1 mg/kg.

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 during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte nebulizer pressures and EGCM settings

Element & wavelength (nm)	Nebulizer pressure (kPa)	EGCM setting
Mg 285.213	180	High
Ca 422.673	240	High
Zn 481.053	120	High
Ba 614.171	240	High
P 213.618	120	Medium

Calibration parameters

The calibration fit and correlation coefficients for the elements analyzed are shown in Table 2. 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. The excellent correlation coefficients demonstrate the capability of the MP-AES to cover the range of concentrations expected in this analysis. The calibration curve for Zn is shown in Figure 1.

Table 2. Analyte calibration fits and correlation coefficients

Element & wavelength (nm)	Calibration fit	Correlation coefficient
Ba 614.171	Rational	0.99908
Ca 422.673	Linear	0.99958
Mg 285.213	Rational	0.99933
Zn 481.053	Linear	0.99999
P 213.618	Rational	0.99998

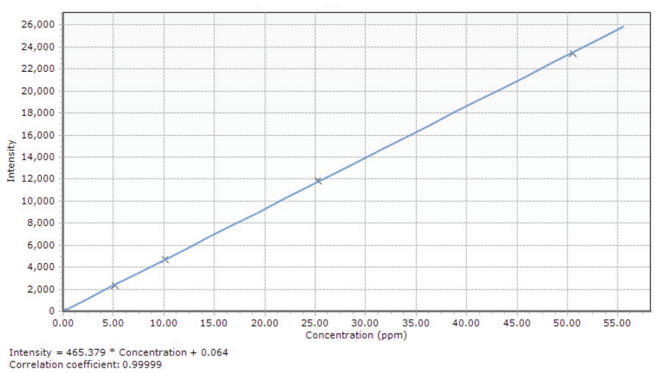

Figure 1. Calibration curve for Zn 481.0.53 nm showing excellent linearity up to 50 ppm with a correlation coefficient of 0.99999

Results and discussion

Analysis of standard reference materials

To test the validity of the method, NIST SRM 1085b was analyzed. The results given in Table 3 show excellent agreement (accuracy) between the MP-AES measured results and the certified values.

Table 3. Measured results versus certified values

Element & wavelength (nm)	Measured concentration (mg/kg)	Certified (mg/kg)	Recovery (%)
P 213.618	301.5 ± 0.1	299.9 ± 7.2	101
Zn 481.053	314.9 ± 0.3	296.8 ± 6.8	106
Mg 285.213	300.6 ± 0.2	297.3 ± 4.1	101
Ca 422.673	279.6 ± 0.1	(298)	94
Ba 614.171	281.2 ± 0.1	300.1 ± 2.4	94

Spike recoveries

The recoveries obtained for the spiked mixed gear oil sample are given in Table 4. Excellent recoveries were obtained for all elements analyzed, demonstrating the validity of the analytical method. The spectrum for Zn is shown in Figure 2.

Table 4. 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 (%)
P 213.618	17.16	26.71	95
Zn 481.053	6.99	17.17	101
Mg 285.213	1.53	11.32	97
Ca 422.673	8.89	19.69	107
Ba 614.171	0.00	9.16	91

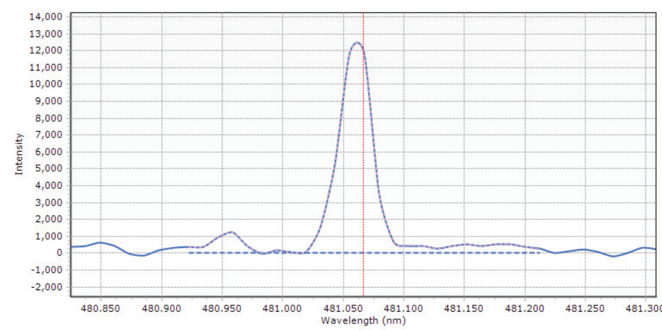

Figure 2. The spectrum for Zn 481.053 nm corrected with Auto background correction

Conclusions

The new Agilent 4100 MP-AES equipped with a OneNeb [1] nebulizer and fitted with the EGCM is an ideal solution for the routine multi-element analysis of additives in oils. The nitrogen-based plasma excitation source exhibits a high tolerance to organic solvent load. 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 on SRM samples and on spike solutions at the 10 ppm level.

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

Published October 12, 2012
Publication number: 5990-8925EN

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