Determination of Wear Metals in Lubricating Oil on The Liberty Series II ICP-OES With the Axially-Viewed Plasma

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-OES) with the axially-viewed plasma is generally used for measuring low levels of metals in clean environmental samples.

The determination of metals in oils by ICP-OES with the radially-viewed plasma is a well known and regularly used technique [1–6]. Due to the widely held belief that axial viewing exacerbates problems with molecular band emissions and carbon build-up when analyzing organic solvents, axially-viewed ICP is not often considered for the analyses of difficult samples such as organic solvents [7]. Recent advances in ICP-OES technology have overcome these problems, so that the axially-viewed ICP can be used with confidence for the analysis of samples dissolved in organic solvents.

The Auxiliary Gas Module 1 (AGM 1) Oxygen Accessory, available from Agilent Technologies, Inc., adds a small volume of oxygen to the argon auxiliary gas. This addition of oxygen reduces molecular band emissions and prevents carbon build-up when organic solvents are analyzed.

The Liberty Series II employs DIrect Serial Coupling (DISC) of the Radio Frequency (RF) generator to the plasma for highly efficient transfer of energy into the plasma. Coupled with the Direct Power Control system which rapidly responds to sample-induced changes in plasma impedance, this produces a stable, robust plasma that is ideal for analyzing difficult samples.

In this study a Liberty Series II spectrometer with an axially-viewed plasma was used for the determination of 13 elements in a standard reference lubricating oil.

Experimental

Instrumental

An Agilent Liberty Series II ICP-OES with the axially viewed plasma and an AGM-1 oxygen accessory were used.

The Liberty Series II ICP features a 40 MHz, free running RF generator, a 0.75 m Czerny-Turner monochromator with a 1800 grooves/mm holographic grating used in up to four orders. The resolution of the optical system ranges from 0.018 nm in 1st order to 0.006 nm in 4th order.

The instrument was controlled with a Digital Equipment Corporation (DEC) Celebris computer with an Intel Pentium processor and Varian Plasma 96 software running under Microsoft Windows 95.

The instrument operating conditions are listed in Table 1.

Table 1. Instrument Operating Conditions

Power	1.5 kW
Plasma gas flow	19.5 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber	Inert Sturman-Masters type with double-pass cyclonic action
Torch	Demountable torch with a 1.8 mm id injector tube
Nebulizer	High flow glass concentric type
Nebulizer pressure	230 kPa
AGM-1 setting	6 turns (170 mL/min)
Pump tube	Inlet - viton, white-white, 1.02 mm id
	Outlet -solvent flexible PVC, grey-grey, 1.30 mm id
Pump rate	10 rpm
Sample uptake rate	0.6 mL/min
Integration time	3 seconds
Sample delay time	60 seconds
Stabilization time	15 seconds
Fast pump	Off
Background correction	Polynomial plotted background
PMT voltage	650 V

A Sturman-Masters spray chamber was used instead of the glass cyclonic spray chamber normally used with this system. The Sturman-Masters spray chamber, which is fully compatible with organic solvents, reduces the solvent load into the plasma resulting in a more stable signal.

Fast pumping during the sample delay time was not used, to avoid the effect of solvent loading on the stability of the signal.

Sample Preparation

The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM)1084a Wear Metals in Lubricating Oil was prepared as a 1 in 100 weight/volume (w/v) dilution in kerosene and shaken well to ensure complete dissolution.

Standard Preparation

Working standards were prepared (w/v) in kerosene from 500 mg/kg Conostan S-21 multi-element organometallic standard. To ensure consistent viscosity, the total oil content in the sample, standards and blank was kept constant (1 in 100 w/v) by adding Conostan neutral base oil 75 as required.

Results and Discussion

Oil Analysis

NIST SRM 1084a Wear Metals in Lubricating Oil sample was analysed to determine the concentration of Al, Ag, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Si, Sn, Ti and V.

Multiple wavelengths were used for some elements as a comparison. The results are listed in Table 2.

Table 2. Results of NIST SRM 1084a

Element	Wavelength (nm)	Measured concentration (mg/kg)	Certified concentration (mg/kg)
Ag	328.068	96.2	101.4 ± 1.5
Al	396.152	96.4	(104)
Al	308.215	96.1	(104)
Cr	267.716	95.7	98.3 ± 0.8
Cu	324.754	99.3	100 ± 1.9
Fe	259.940	99.3	98.9 ± 1.4
Mg	279.553	97.3	99.5 ± 1.7
Mg	280.270	97.4	99.5 ± 1.7
Mo	281.615	97.9	100.3 ± 1.4
Ni	221.647	99.8	99.7 ± 1.6
Pb	220.353	99.1	101.1 ± 1.3
Pb	261.418	99.4	101.1 ± 1.3
Pb	283.306	100.4	101.1 ± 1.3
Si	251.611	96.3	(103)
Si	288.158	97.0	(103)
Sn*	189.926	101.2	97.2 ± 2.6
Sn*	235.484	101.8	97.2 ± 2.6
Ti	334.941	99.5	100.4 ± 3.8
V	292.402	100.0	95.9 ± 9.4
V	309.311	100.5	95.9 ± 9.4

*Significant contamination was present in the solvent.
Values in parenthesis are not certified.

The measured values are in good agreement with the certified values. The precision of the measurements ranged from 0.1 to 1.5% Relative Standard Deviation (RSD).

Long Term Stability

Long term stability was evaluated by performing a calibration and then analysing the sample continuously. Over two hours, the reproducibility ranged between 0.2 to 1.3 %RSD. The plots of the long term stability for the elements Ni, Cr and Cu are displayed in Figure 1.

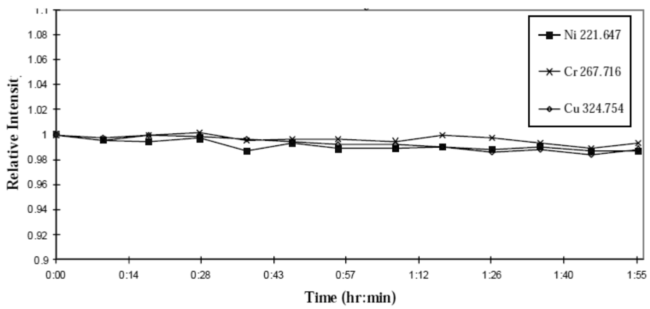

Figure 1. Stability of results for Ni, Cr and Cu in kerosene on the Liberty Series II. ICP-OES with the axially-viewed plasma.

Detection Limits in Kerosene

Detection limits (3 sigma) for a number of elements in kerosene were measured on the Liberty Series II ICP-OES with the axially-viewed plasma and compared with those obtained on an ICP-OES with a radially-viewed plasma [1].

The results are listed in Table 3.

Table 3. Detection Limits in Kerosene

Element	Wavelength (nm)	Axial ICP detection limit (µg/L)	Radial ICP detection limit [1] (µg/L)
Ag	328.068	1.0	3.9
Al	396.152	11	3.0
Al	308.215	3.0	–
Cr	267.716	0.4	–
Cu	324.754	0.5	1.8
Fe	259.940	1.7	1.9
Mg	279.553	0.2	3
Mg	280.270	0.2	–
Mo	202.030	1.4	14
Mo	281.615	0.7	–
Ni	231.604	3.3	10
Ni	221.647	0.6	15
Pb	220.353	3.1	60
Pb	261.418	6.2	–
Pb	283.306	8.7	77
Si	251.611	0.7	4.5
Si	288.158	2.1	–
Ti	334.941	0.2	0.9
V	292.402	0.5	3
V	309.311	0.2	–
B	249.773	2.1	5.3
B	249.678	5.0	7.5
Cd	214.438	0.1	–
Cd	226.502	0.2	–
Cd	228.802	0.3	3
P	213.618	3.9	18
Zn	213.856	0.4	2.7
Zn	206.200	0.4	–

Detection limits with the axially-viewed ICP are generally better by factor of up to 10 compared to the radially-viewed ICP. Some elements, such as Pb and Ni, had an improvement of 20 to 25 fold.

The detection limit of Al 396.152 nm was higher on the axially-viewed ICP because of molecular band emission. The detection limit was better lower for the less sensitive Al 308.215 nm line and was similar to that determined for the Al 396.152 nm line on the radially-viewed ICP.

Due to the presence of contamination in the solvent, the detection limit of tin was not determined.

Summary

Trace metals in lubricating oil can easily be determined on the Liberty Series II ICP-OES with the axially-viewed plasma.

By using the AGM-1 Oxygen Accessory, improvements in detection limits were observed compared with the radially-viewed ICP. Short-term precision and long-term stability were also found to be excellent because of the elimination of carbon build-up.

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