Determination of Metals in Lubricating Oil by ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Authors

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Introduction

Metals in lubricating oil can come from various sources, such as wear, contamination and additives. Wear metals result from friction or corrosion of the engine components, for example, pistons, and bearings, during operation. Contamination can come from dirt, leaks or residual metal pieces. Additives used as detergents, anti-oxidants, and anti-wear agents, are added in order to reduce engine wear.

Regular monitoring of wear metals in oil can diagnose engine wear, so that preventive maintenance procedures can be performed, increasing equipment reliability. The analysis of oils for trace metals is routinely carried out as an equipment maintenance program for engines of various types.

Inductively Coupled Plasma Atomic Emission Spectroscopy is an efficient technique in the application of oil analysis and has been studied by several workers [1–7]. This article describes the determination of 21 elements in an oil sample by ICP-OES.

Agilent Technologies

Experimental

Instrumental

An Agilent Liberty 100 Inductively Coupled Plasma Optical Emission Spectrometer, featuring a 40.68 MHz RF generator, a 0.75 m Czerny-Turner Monochromator with a 1800 grooves/mm Holographic grating, was used. The resolution of the optical system is 0.018 nm in 1st order, 0.009 nm in 2nd order, 0.007 nm in 3rd order and 0.006 nm in 4th order. The instrument was controlled by an IBM Personal Computer PS/2 Model 30/286.

The instrument operating parameters are listed in Table 1.

Table 1. Instrument Operating Conditions

Power	1.5 kW
Plasma gas flow rate	12.0 L/min
Auxiliary gas flow rate	2.25 L/min
Torch type	Standard one piece quartz torch with 1.4 mm id injector tube
Nebulizer type	Glass concentric K
Nebulizer pressure	120 kPa
Pump tube type	Solvent flexible
Pump tube	White-white (inlet) Red-red (outlet)
Pump rate	15 rpm
Sample uptake rate	1.1 mL/min
Integration time	3 sec
Viewing height	Optimized for SBR
Background correction	Dynamic
PMT voltage	650 V
Grating order	Default
Filter position	Default

For optimum operation when running organics, the torch was lowered by 1 mm compared with the normal aqueous position. This means that the distance between the bottom of the load coil to the top of the intermediate tube was 3 mm (compared to 2 mm for running aqueous).

Another parameter that differed from running aqueous solution was the nebulizer pressure. Because the introduction of an organic solvent changes the characteristic of the plasma, a green "tongue" is apparent in the lower region of the aerosol channel which results from molecular C_2 emission (Swan bands). The optimum nebulizer pressure is set by adjusting the green "tongue" so that the top of the tongue is about 1 mm above the top of the torch. The nebulizer pressure varies depending on the solvent type. In this experiment, the nebulizer pressure was set at 120 kPa which compares to 170 kPa while running aqueous solution.

To minimize any potential carbon build up on the rims of the two inner tubes and the injector tip of the torch, the auxiliary gas flow was set to 2.25 L/min.

It is important to note that, because the amount of solvent load into the plasma is limited, different solvents have different limiting aspiration rates [8]. For example, the limiting aspiration rate is 4 mL/min for xylene and 3 mL/min for MIBK. Exceeding the limit could result in degradation of plasma stability, leading to carbon build up at the torch, and ultimately the plasma will extinguish. It was necessary to use the optimum sample uptake rate. The use of "Fast pump" is not recommended during the run.

Sample Preparation

Because of the possible difference in viscosity between oil samples, it may be necessary to dilute the oil sample with an organic solvent which is completely miscible with the oil sample. The solvent should be of low viscosity, free of analyte impurity, and have low vapor pressure and high boiling point. The solvents which are commonly used are: Xylene, Kerosene, DIBK, MIBK or White spirit. The dilution can be prepared either on a weight per weight or weight per volume basis, and a 1/10 dilution is normally applied. However, it is up to the analyst to decide the appropriate dilution factor for the particular analysis.

Wear metals are typically present in oil as metallic particles rather than dissolved in the oil. The particle size and concentration of individual wear metals in oil differ from one element to another and depend engine type, the age of the oil and the efficiency of the oil filter.

In normal operation, most wear metal particles are much less than 1 µm [9]. Metallic particle size distribution can affect the accuracy of the analysis. The dilution method is only applicable for wear metal particles up to 5 µm. For larger particle sizes, an acid digestion method has to be applied [3,4].

In this experiment, the oil sample was ultrasonicated for 5 minutes. The sample was then diluted 1/10 w/v with kerosene and shaken well to ensure complete dissolution.

Standard Preparation

Working standards were prepared in w/v with kerosene from Conostan S-21 multi-element organometallic blended standard (Conostan Division, Continental Oil Company, Ponca City, Oklahoma, USA) with 21 elements and each had a concentration of 500 ppm in hydrocarbon oil. Due to the linear dynamic range of the instrument, a two point calibration is sufficient when the working standard is a 50 ppm multi-element solution.

In order to ensure consistent solution viscosity, the total oil content in samples, standards and blank should be constant. A neutral base oil was used to make up for any differences. It is recommended that the same brand used in the engine be used for this purpose, to give better accuracy at low levels. In this experiment 10% w/v Conostan neutral base oil 75 was added to the blank solution.

Analytical Conditions

The analytical wavelengths were selected based on the minimum potential spectral interferences and maximum analytical performance. For example, in selecting the wavelength used for B, as illustrated in Figures 1 and 2, the Fe line interferes with the B 249.773 nm line, but resolves well with the B 249.678 nm line. Therefore, if the Fe content in the sample is low the B 249.773 nm line is used, while if the Fe content is high the B 249.678 nm line is used.

Less sensitive lines were chosen as the additives Ba, Ca, Mg are normally present in high concentrations.

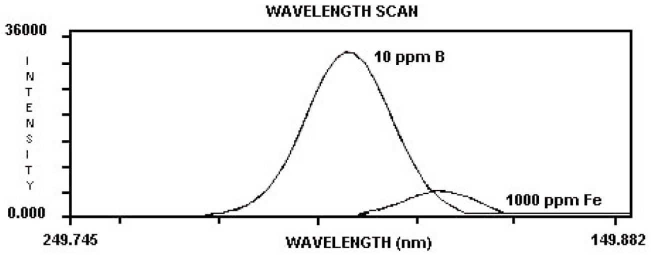

Figure 1. The effect of 1000 ppm Fe on 10 ppm B at the B 249.773 nm line.

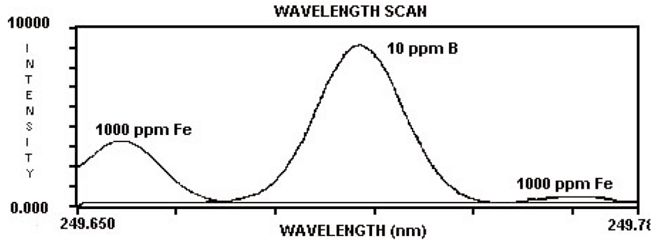

Figure 2. The effect of 1000 ppm Fe on 10 ppm B at the B 249.678 nm line.

Spectral interferences from molecular band emission are not generally significant when running aqueous solutions. When organic solvents are introduced, molecular bands such as C_2 (Swan), CN (violet), and CH appear in the wavelength region higher than 330 nm [8]. These cause structural background, and hence dynamic background correction is required. Figures 3 and 4 show the background emission for a kerosene blank and a water blank at Cu 324.754 nm and Al 396.152 nm respectively.

The analytical wavelengths and detection limits are listed in Table 2.

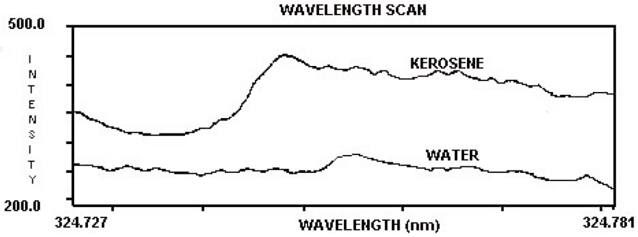

Figure 3. Background emission of kerosene blank and water blank at Cu 324.754 nm.

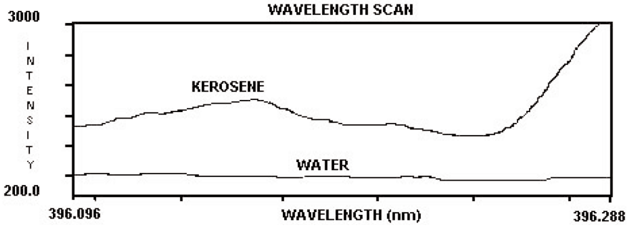

Figure 4. Background emission of kerosene blank and water blank at Al 396.152 nm.

Table 2. Detection Limit in Kerosene

Element	Wavelength nm	Detection limit ng/mL
Ag	328.068	2.6
Al	396.152	2.0
B	249.773	3.5
B	249.678 (alternate)	5.0
Ba	233.527	1.1
Ca	317.933	2.8
Cd	228.802	2.0
Cr	283.563	1.2
Cu	324.754	1.2
Fe	259.940	1.3
Mg	285.213	2.4
Mn	260.569	0.6
Mo	202.030	9.6
Na	589.592	6.8
Ni	231.604	6.5
Ni	221.647 (alternate)	10.0
P	213.618	12.0
Pb	220.353	40.0
Pb	283.306 (alternate)	51.0
Si	251.611	3.0
Sn	189.926	32.0
Ti	334.941	0.6
V	292.402	2.0
Zn	213.856	1.8

Results

A known amount of each analyte was added to the sample, and percentage spike recoveries were measured and are listed in Table 3.

Table 3. Percentage Spike Recovery of the Analysis

Element	%Recovery
Ag	100
Al	101
B	104
Ba	95
Ca	100
Cd	96
Cr	96
Cu	94
Fe	98
Mg	95
Mn	96
Mo	101
Na	92
Ni	99
P	98
Pb	96
Si	97
Sn	102
Ti	98
V	97
Zn 1	00

The precision of the measurements ranged from 0.1 to 0.9 %RSD.

Conclusion

The determination of trace metals in lubricating oil by ICP-OES has been performed with a simple 1/10 w/v dilution with kerosene. The percentage spike recoveries obtained ranged from 92 to 104% with relative standard deviation from 0.1 to 0.9%. The measured detection limits for 21 elements in kerosene were so low that most of the elements are determinable at typical levels present in lubricating oils.

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