Wear Metals and Additive Elements Analysis in Used Lubricating Oils Using ICP-OES

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Lubricating oils are used in very difficult conditions in engines reaching high temperatures and varying pressure conditions in contact with many metallic parts. The lubricating function of the oil can be modified according to the amount and the nature of the metals present. The analysis of used oil is an effective tool to ensure the control of the lubricating function of the oil. Moreover, monitoring the wear metals content can be used as a diagnostic to schedule preventive maintenance. In fact, preventive maintenance will reduce the cost directly linked to materials and parts but also due to down-time. Any harm or damage that may result from an engine failure may also be avoided.

The robustness of ICP-OES and its ability to handle organic solvents and to analyze many elements make this technique the best choice to perform such diagnostics. A simple dilution of the sampled oil in an organic solvent, as kerosene, has to be done so no tedious sample preparation is necessary and the analysis is performed within a few minutes.

Wear metal	Possible sources
Al	Engine block, Pistons, Blowers, Oil pump bushings, Bearings, Oil cooler
B	Coolant leak, Grease contamination
Ca	Grease contamination
Cr	Cylinders, Piston rings
Cu	Bearings, Oil cooler core
Fe	Cylinders, Piston rings, Valve train, Engine block, Oil pump, Rolling elements, Bearings, Spring gears
Pb	Bearings, Gasoline contamination (leaded gasoline)
Si	Engine block, Dust from breathers
Sn	Bearings, Oil cooler core, Connecting rods

Table 1: Wear metals and possible sources

Additive element	Function
B	Corrosion inhibitor, Anti-wear, Anti-oxidant
Ba	Corrosion inhibitor, Detergent, Rust inhibitor
Mg/Ca	Detergent/Dispersive additive
Mn	Combustion Improvement and smoke suppression in residual and distillate oil
P	Anti-wear, Corrosion inhibitor, Anti-oxidant
S	Component of many additives
Si	Defoamant additive
Zn	Anti-wear, Corrosion inhibitor, Anti-oxidant

Table 2: Additive elements and their function

According to the metals content and to the trends observed by the elemental monitoring, faulty parts and lubricating power decrease can be identified for preventive maintenance. The standard method ASTM D5185, describing the analysis of 22 elements, is suitable for the analysis of the additive elements as well as the wear metals in used lubricating oils. Wear metals analysed and their potential origins are given in Table 1 while additive elements and their role are given in Table 2. Some elements are used as both additives and wear metals. Monitoring their content is then crucial as a decreasing or an increasing value will induce different actions.

Instrument

An ACTIVA S ICP spectrometer from HORIBA Scientific, figure 1, was used to perform the analysis. This instrument has been especially designed for reduced operating costs and high performance.

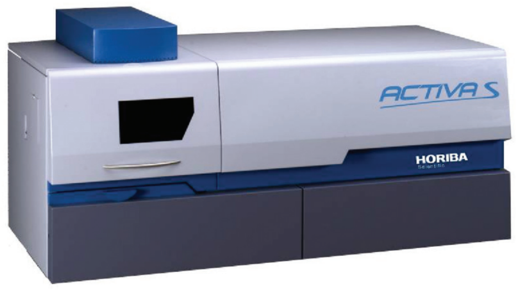

Figure 1: ACTIVA S

HORIBA Scientific ICP spectrometers historically use a vertical torch with radial viewing. Vertical torches offer a more robust configuration than axial systems, allowing the analysis of the most complex matrices. Moreover, using radial viewing of the plasma has several advantages such as drastically reducing matrix effects and molecular emission based spectral interferences. Carbon build-up is also avoided with the vertical position of the torch and ensures long-term stability with organic solvents.

To improve sensitivity, HORIBA Scientific ICP spectrometers use a 3 mm internal diameter injector. The residence time of the sample into the plasma is increased, facilitating the energy transfer between the plasma and the sample, thus reducing any potential matrix effects. Unrivaled sensitivity is also obtained thanks to the Total Plasma View concept, only possible with the high quality optics of the spectrometer. The whole Normal Analytical Zone, figure 2, where all atoms and ions are emitting their wavelengths, is measured. The optics and the CCD detector are designed to fit this 7 mm high zone which is imaged on the entrance slit.

The CCD detector is a Megapixel detector with 1024 x 256 pixels allowing the measurement of large spectral windows and the whole Normal Analytical Zone. The ultra low noise and the low dark current of the CCD allow the detection of weak signals, even for short integration times and the dynamic range is increased as the light is split between many pixels in a column.

As well as the ICP spectrometer, the introduction system used has been especially designed for wear metals analysis. The nebulizer is made of a unique 1 mm i.d. Inox needle, Figure 2, and used with a Scott type spray-chamber. The nebulizer can handle organic solvents even with undissolved particles, which may often be observed in used oils. The robustness of the method is then greatly improved by eliminating the risk of nebulizer blockage. This introduction system is combined with the standard fully demountable torch and the unique sheath gas device for enhanced stability and reduced memory effects.

Figure 2: 1 mm HORIBA Jobin Yvon nebulizer

Standards and sample preparation

Reagents

Kerosene, base oil 75 and multi-element organometallic oil standards at 900 ppm and 500 µg/g were used. Following elements are present in the standards: Al, Ba, B, Cd, Ca, Cr, Cu, Fe, K, Pb, Mg, Mn, Mo, Ni, P, Si, Ag, Na, Sb, Sn, Ti, V and Zn.

Base Oil was used to prepare a blank sample for the calibration and also to ensure a constant amount of oil for all solutions, minimizing the differences of viscosity between samples.

All standards solutions including the Base Oil were supplied by Spex Certiprep.

Standards

A blank was prepared by weighing 5 grams of base oil 75 made up to 50 mL with kerosene.

900 ppm organometallic standard was used to prepare the calibration standards at 10, 20 and 50 ppm for all elements. Thus, 0.555 g, 1.111 g and 2.775 g of

Element / Line	Conc ppm	RSD %	Recovery %
Ag 328.068	29.2	0.1	97
Ag 338.289	29.1	0.3	97
Al 308.215	29.9	0.7	99
Al 309.271	29.7	0.7	99
B 249.677	29.4	0.6	98
B 249.773	29.9	0.7	99
Ba 233.527	29.6	0.6	98
Ca 315.887	29.7	0.9	99
Ca 317.933	30.3	1.1	101
Cr 205.571	30.2	0.2	100
Cu 327.395	28.8	0.2	96
Fe 259.837	29.4	0.2	98
Fe 259.940	29.4	0.2	98
K 766.490	29.3	1.0	97
Mg 279.800	31.2	0.3	104
Mg 285.213	29.8	0.3	99
Mn 257.610	30.0	0.3	100
Mn 293.931	30.0	0.5	100
Mo 202.030	29.5	0.3	98
Mo 281.615	30.3	0.5	101
Na 589.592	28.9	0.4	96
Ni 231.604	30.1	0.5	100
P 177.433	29.7	0.3	99
P 178.221	29.9	0.5	100
Pb 220.353	31.5	0.1	105
S 180.669	30.8	1.0	103
Si 251.611	31.6	0.7	105
Si 288.158	30.8	0.2	103
Sn 242.949	30.0	0.4	100
Ti 334.941	29.7	0.3	99
Ti 337.280	29.6	0.3	99
V 292.402	29.7	0.5	99
V 292.464	29.7	0.5	99
V 309.311	29.4	0.5	98
V 311.071	30.0	0.6	100
V 311.838	30.2	0.8	100
Zn 202.548	31.2	0.2	104
Zn 206.200	30.6	0.3	102

Table 4: Results and recoveries obtained on the check standard

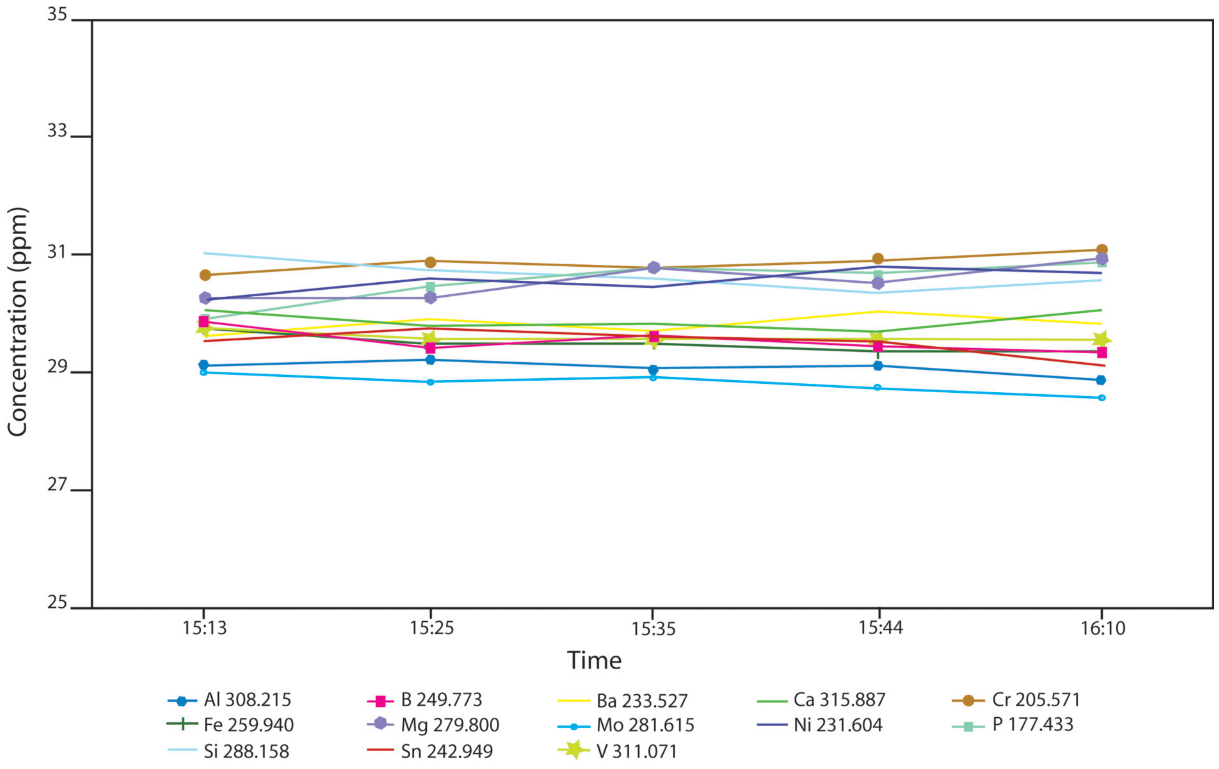

Figure 3: Concentrations of check standard over 1 hour

standard were accurately weighed and made up to 5 grams with base oil 75. The resulting solution was diluted to 50 mL with kerosene.

Samples

500 ppm organometallic standards were used to prepare the check standard at 30 ppm for all elements. Thus, 6 g of standard was accurately weighed and made up to 10 grams with base oil 75. The resulting solution was made up to 100 grams with kerosene.

Parameter	Setting
Power	1200 W
Plasma Gas	14 L/min
Auxiliary gas	0.8 L/min
Sheath gas	0.2 L/min
Nebulizer flow	0.5 L/min
Torch Injector diameter	3 mm
Pump speed	15 rpm
Pump tubing	Black-Black Viton for sample Grey-Grey Viton for drain
Spray chamber	Scott
Nebulizer	HORIBA Jobin Yvon 1 mm nebulizer

Table 3: Instrument parameters

Experimental

Method development

Wavelengths were selected accordingly to the recommendations of ASTM D5185. To take full benefit of the CCD detection, several wavelengths were used for most of the elements. The confidence in the final result is thus improved and potential spectral interference can be easily identified during the analysis.

All the gas flows were optimised to obtain stable plasma with the base of the plasma located 1 mm beyond the coil. The Nebulization gas flow was optimised to obtain a central channel that is approximately 3 mm high from the load coil. Thanks to the Total Plasma View concept, there is no need to optimize the viewing height as all emission lines will be simultaneously observed. All parameters and settings are given in Table 3.

It was checked that no spectral interferences occur on standards and background correction was done using the Advanced Background Correction. This type of background correction is automatically performed by the system on the basis of the shape of the signal and its vicinity. There is no need for the analyst to set or to re-position the background correction position, eliminating the need to check spectra for many samples. Method development and analysis are thus simplified.

Analytical results

The calibration was performed using the 10, 20 and 50 ppm standards and the check standard at 30 ppm was analyzed in a single run. The concentration obtained was compared to the expected concentration and recoveries were calculated for all the wavelengths measured. Results are given in Table 4.

The results are consistent for all elements and all lines with low RSDs, proving the short term stability of the instrument. The reliability is confirmed by the excellent recoveries obtained, which within statistical variations are essentially 100% (less than 5% deviations from the expected concentration), even for difficult element in organics such as alkali elements.

Stability

Stability on organic matrices is often more difficult to achieve than on aqueous standards due to the volatility of the sample and to the high density of the aerosol created. The amount of carbon introduced into the plasma is also asking for enhanced robustness of the generator and the plasma torch to ensure stability. To evaluate the stability of the ACTIVA S on the analysis of wear metals in oils, the check standard was analysed several times on a one hour basis. Results obtained are displayed in Figure 3. The obtained concentration was directly plotted as a function of time displaying the raw stability of the system.

Excellent stability was achieved ensuring long term stability for oil analysis, proving the ability of the ACTIVA S to produce accurate and stable results on samples, without needing routine periodic recalibration.

Conclusion

As proved by the accuracy and the stability obtained on the samples analyzed, wear metals analysis can be performed easily using the ICP spectrometer following the recommendations of ASTM D5185.

The vertical torch and the radial viewing mode ensure enhanced robustness as well as reduced interferences, particularly for organic solvents matrices. The method robustness is greatly improved with the special nebulizer designed for wear metals analysis that suppresses the potential blockage issue that can occur with many standard nebulizers due to the particles often observed in used oils.