Application Note: 40757

Determination of wear metals and additive elements in used lubricating oils

Key Words

- ICP
- iCAP 6300 Radial
- Additive elements
- Internal standard
- Lubricating oils
- Wear metals

Introduction

Modern lubricating oils contain a complex mixture of organometallic compounds, which are added to the base oil to improve its anti-wear and anti-oxidative characteristics. To ensure consistent production quality it is necessary to monitor the concentration in finished oil products as it is manufactured, and over its lifetime. ICP is a very effective tool in the automotive and ancillary industries for the determination of these wear metals and additive concentrations as it offers many advantages over other techniques such as: high temperature source allowing for dissociation and determination of all elements, robust generator to analyze organics directly, and it is a fast multi element technique. The presence of various elements and their increasing/decreasing levels can indicate the type of wear that an engine is subject to e.g. the presence of Aluminium in an engine oil may be due to wear of the pistons and gear casings. The determination of these elements is essential for the efficient scheduling of maintenance, and early detection of wear and tear on engine parts. Wear metals are also analyzed by the end user, as the decrease in concentration of additives will lead to loss of its lubricating qualities and subsequent failures in machinery.

ELEMENT	POSSIBLE SOURCE OF ELEMENT
Al	Pistons, push rods, bearings (Al-Sn), air coolers, gear casings
Cr	Cylinder liners, piston rings, alloy steel valves
Cu	Bearing, bushes (Cu-Pb-Sn), coolant core tubes
Fe	Piston rings, ball/roller bearings, gears, valves guides
Pb	Fuel contamination, bearings (Pb-Sn), housings
Si	Dust, seal materials, silicon lubricant (jet engine)

Table 1: Sources of wear metals

Principle[1] [2]

Samples should be collected in dry acid washed containers whilst the oil is still warm and circulating. To avoid contamination from tooling used during collection, the first portion should be discarded. The samples are then diluted in kerosene.

Instrumentation

An iCAP 6300 Radial ICP was chosen for the analysis. The iCAP 6000 series is the first generation of Thermo Electron Corporation's new breed of ICP emission spectrometer, designed specifically for low cost of ownership through low gas flows and the smallest footprint of any ICP on the market.

It employs a high-resolution Echelle spectrometer with a much improved charge injection device (CID) detector. Advancements in CID technology allow this detector to feature higher sensitivity and lower noise than any of its predecessors. The radial view plasma was selected to reduce matrix interference.

PARAMETER	SETTING
Pump Winding	Orange/white viton sample White/white viton drain
Pump rate	25 rpm
Nebulizer	v-groove
Nebulizer Argon Pressure	0.2 MPa
Spray Chamber	organics
Center tube	1.0 mm
Torch Orientation	Radial
RF Forward Power	1150 W
Purge Gas	Argon
Coolant flow	14 L/min
Auxiliary flow	1.0 L/min

Table 2: Instrument Parameters

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Method

Reagents

Kerosene, S21 Conostan Oil based standard- 900 ppm mixture of Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn.

Standard Reference Materials:
Wear metals in lubricating oil SRM1084a
Wear metals in lubricating oil SRM1085b
Blank Oil

All reagents/reference materials supplied by:
LGC Promochem, Queens Road, Teddington, Middlesex TW11 0LY, United Kingdom.

Sample Preparation

Samples were warmed to 60 °C and mixed thoroughly before use. 5 g of sample oil was weighed into a 50 ml volumetric flask and made up to the mark with diluent.

The diluent was kerosene with no additives or internal standards. The same batch of kerosene was used in the standard and sample preparation. A constant oil to kerosene ratio is maintained to minimize viscosity effects.

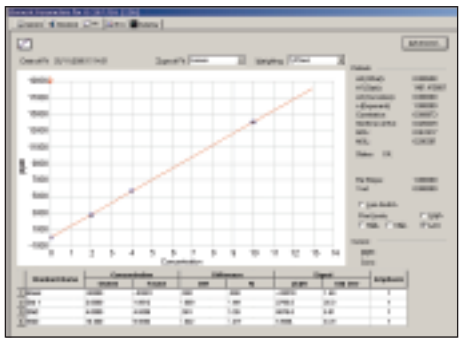

Figure 1: Calibration Curve for Cr

Standard Preparation

High purity Conostan standards were used to prepare the calibration standards for this method. 0.555 g, 1.111 g and 2.775 g of Conostan S21 (900 ppm) was accurately weighed, and made up to 5 grams with blank oil. This was then diluted to 50 ml in each case, which corresponds to 10, 20 and 50 ppm for all elements.

Method development

Variations in viscosity were minimized with a large dilution of 5 g of sample up to 50 ml with kerosene. In addition, blank oil was used to make up the mass of standards to the same mass of oil as the samples, further minimizing viscosity differences.

Measurements were taken of each standard, sample and blank and the subarray plot for each element examined. It is from here that the center and background points for each element were examined, and re-positioned if necessary.

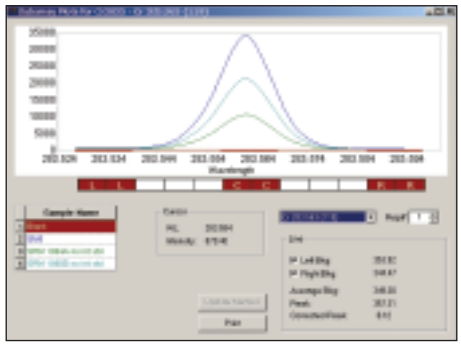

Figure 2: Subarray plot showing integration and background points

	SRM1084A (ppm)		SRM1085B (ppm)		MDL (ppb)
ELEMENT	**FOUND**	**CERT.**	**FOUND**	**CERT.**	
Ag 338.289	98.7	101.4 ± 1.5	311.2	304.6 ± 8.9	11.9
Al 308.215	101.7	104 *	298.8	300.4 ± 9.3	33.7
Ba 233.527			305.1	300.1 ± 2.4	1.2
Ca 315.887			298.7	298 *	12.6
Cd 214.438			298.8	302.9 ± 5.1	0.5
Cr 267.716	99.6	98.3 ± 0.8	304.0	302.9 ± 3.9	11.6
Cu 224.700	100.3	100.0 ± 1.9	297.8	295.6 ± 8.5	4.1
Fe 238.204	101.5	98.9 ± 1.4	298.7	301.2 ± 5.0	9.8
Mg 279.079	101.3	99.5 ± 1.7	296.4	297.3 ± 4.1	53.9
Mn 293.930			303.7	300.7 ± 2.0	9.5
Mo 202.030	99.4	100.3 ± 1.4	295.3	300.6 ± 3.2	3.8
Na 589.592			295.6	305.2 ± 7.0	35.6
Ni 231.604	100.4	99.7 ± 1.6	298.7	295.9 ± 7.0	3.2
P 178.284			299.7	299.9 ± 7.2	23.0
Pb 220.353	100.8	101.1 ± 1.3	298.9	297.7 ± 6.8	14.4
Si 288.158	100.7	103 *	299.8	300.2 ± 5.0	18.6
Sn 189.989	99.2	97.2 ± 2.6	293.1	299.4 ± 4.8	10.1
Ti 323.904	102.4	100.4 ± 3.8	299.3	301.1 ± 2.9	9.7
V 268.796	101.8	95.9 ± 9.4	292.1	297.8 ± 4.6	10.5
Zn 206.200			297.6	296.8 ± 6.8	1.0

* Not certified value, for information only

Table 3: Results

Determination

The instrument was calibrated using one blank and three standards, after inspection a linear fit was applied to all elements. Samples were analyzed in a single sequence. The sample data was measured by interpolation and results are shown in Table 3 above. The Method detection limit was analyzed and results are also in Table 3.

Conclusions

Rapid, precise, accurate results for additives and wear metals are easily attained on the iCAP Radial ICP. The analysis with the iCAP 6300 Radial produced accurate, precise results with excellent long term stability and detection limits. The full wavelength coverage of the unique CID detector allowed the optimum wavelength to be selected while the high tolerance and sensitivity of the radial torch provided freedom from interference and the lowest possible detection limits for this application.

References

1) ASTM D4951-02, Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

2) ASTM D5185-02e1, Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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