Classification analysis of metals in engine oil

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Instrument: ULTIMA 2

1 Introduction

Diagnosis of the deterioration degree of engine oil is generally evaluated by infusible components, viscosity and oxidation. For abrasion examination, an analysis of metals in engine oil is carried out with an ICP atomic emission spectrometer. The common procedure, such as described in the ASTM D 5185, consists of a 10 times dilution of oil in kerosene (or xylene) with organic-based operating conditions for the plasma and sample introduction parameters (use of wear metals in oil dedicated nebuliser: JY 1 mm Pt stainless steel needle). The main target is to control the oil over its use life, by a relative comparison. If reproducibility of the method is ensured, estimation of wear metals in oil is then performed on a routine basis.

This application flash describes the analysis of metals from another approach, using the ULTIMA 2 ICP-AES instrument.

2 Operating conditions

Samples can present large particulates when wear metals are present in used oils. With the use of the JY nebuliser featuring a 1 mm id sample needle, accuracy of metals analysis in oil and particulates is easily achieved.
The study here is to estimate the proportion of metals in the oil and in the particulates, and to observe how it evoluates.

• Sample preparation
10 g of sample is weighted in a beaker and diluted with Xylene solvent. The solution is then filtered with a filter paper of No.5C (cellulose filter paper, Advantec Toyo Kaisha), and diluted to 50 g with Xylene (analytical grade). The filter paper containing metal particulates whose diameter is > 1 µm, is transferred into a platinum crucible, to be ashed in a furnace at 600 °C. After cooling, the residual substance in the platinum crucible is mixed with 3 mL of nitric acid (analytical grade), heated and transferred into a beaker. 2 mL of hydrochloric acid (analytical grade) is added, and the solution is heated again to get complete dissolution. After cooling, this sample solution is diluted to 20 mL with de-ionised water.

The filtered solution is named "Solution A". The solution after filter + particulates digestion is named "Solution B".

Standards for solution A analysis are prepared from organo-metallic Spex Certiprep standards, using Base Oil and Xylene as solvent. Base Oil + organo-metallic amounts must match the proportion of oil in solution A (20 %).
Standards for solution B are prepared from Précis standard solutions (HORIBA Jobin Yvon), in de-ionised water.

• ULTIMA 2 Specifications

Table 1: Specifications of the ULTIMA 2 ICP spectrometer

Parameter	Specification
Generator	40.68 MHz, solid state, water-cooled
Optical System	Czerny-Turner (1 m Focal)
Gratings	2400 g/mm double order
Spectral range	120 - 800 nm (Far UV option)
Resolution	5 pm in 120 - 320 nm range 10 in 320 - 800 nm range
Plasma view	Radial*
Torch design	Vertical demountable, 3 mm i.d injector

* Total Plasma View (observation of the complete NAZ, Normal Analytical Zone), for minimised matrix effects and optimum sensitivity.

• Plasma parameters
For solution A analysis, the dedicated JY organic nebuliser is used (with Pt sample needle of 0.7 mm i.d.), mounted in a Scott spray chamber (glass). Nebuliser pressure is fixed at 2 bars. Pump tubings are Solvflex made (black/black for sample and grey/grey for drain).

For solution B, a standard aqueous sample introduction system is used, based on a concentric nebuliser and cyclonic spray chamber (glass), with Tygon pump tubing (black/black for sample and grey/grey for drain).
Plasma parameters are listed in Table 2.

Table 2: Plasma parameters for analysis of solutions A and B

	For sample A Xylene sample	For sample B Water solution
Generator power (kW)	1.2	1.0
Plasma gas flowrate (L/min)	18	12
Auxiliary gas flowrate (L/min)	1.2	0
Sheath gas flowrate (L/min)	0.2	0.2
Nebuliser (L/min)	0.5	0.8

3 Analytical results

Two different oil samples were analysed: sample 1 which is the clean oil before use, and sample 2, the same oil after 2000 hours of use in an engine.
The same sample preparation (filtering (solution A) and digestion (solution B)) was applied for both samples 1 and 2. Results are listed in Table 3.

• Results

The limits of detection are estimated using the formula LOD = 3 x SD. SD is the Standard Deviation of the blank concentration from an analysis of 10 replicates.

Table 3: Results of 2 oil samples (clean and used) with both sample preparations (unit is ppm).

	Sample 1 The concentration in oil before use			Sample 2 The concentration in oil after 2000 hours use		
	Solution A	Solution B	Total	Solution A	Solution B	Total
P	120	10	130	118	11	129
S	24	0.2	24.2	24.5	0.3	24.8
Sn	2.3	0.15	2.45	4.4	0.3	4.7
Zn	5.6	0.3	5.9	6.5	0.62	7.12
Pb	1.5	0.2	1.7	2.3	0.38	2.68
Ba	0.82	0.10	0.92	0.85	0.08	0.93
B	172	5.3	177.3	170	6.0	176
Si	10.5	1.5	12	12.3	3.2	15.5
Mn	0.24	0.02	0.26	0.38	0.32	0.70
Fe	19.5	1.5	21.0	37.8	28.1	65.9
Cr	0.21	0.1	0.31	0.402	0.25	0.652
Mg	1.45	0.15	1.60	1.54	0.12	1.66
Cu	40.5	1.8	42.3	67.7	3.5	71.2
Ca	166	4.5	170.5	165	5.0	170
Al	15.2	1.1	16.3	27.3	10.6	37.9

• Observations

The concentration of iron in engine oil generally rises with increasing use. It illustrates the deterioration of lubrication performance of the engine oil.
For sample 2, the concentration is still at a normal level.
In addition, in recent years, Al - Sn - Si alloys are used as bearings for small engines. This can explain the increase of their concentration in sample 2.

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