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APPLICATION NOTE 44426

Lubricating oil analysis according to ASTM D5185 using the Thermo Scientific iCAP PRO XP ICP-OES

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Goal

This application note describes the analysis of lubrication oils in accordance with standard test method ASTM D5185 for "Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by ICP-OES".

Introduction

The cost of unscheduled maintenance of engines and machinery can be high, not only in materials and labor, but also in lost profits due to downtime. Therefor the analysis of used lubricating oil for wear metals, contaminants and additive elements is a valuable diagnostic tool to schedule preventative maintenance. Once the oil has been sampled, analysis by ICP-OES is very useful for aiding with maintenance scheduling, basing decisions on the results of analysis. The high temperature source of an ICP-OES, which dissociates any organometallic compounds and also its ability to handle difficult organic solvent matrices makes the ICP-OES an ideal technique. This allows the oil to be directly aspirated into the instrument after a simple dilution, negating the need for any time consuming digestion sample preparations and consequently enabling faster turnaround times.

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Standard method ASTM D5185

Scope

The standard method ASTM D5185 is for "Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by ICP-OES". A total of 22 elements can be determined by this test method and it is generally used as a rapid screening method to monitor the condition of the equipment using the oil and to define when preventative action is needed. The metallic analytes must be oil soluble for accurate quantification. The quantification of insoluble particles such as small particles (greater than a few micrometers) of metal dislodged from a mechanical part is not possible when using this method and any attempt to do so will result in low recoveries. This is due to the plasma not fully atomizing larger particles. It should also be highlighted that obtaining a representative sample would be difficult in such cases.

Summary of test method

An aliquot of a homogenized sample is diluted by weight with a suitable solvent (such as mixed xylenes). Standards are prepared in the same manner. The concentration of metals within a sample is then determined by direct analysis using ICP-OES.

Instrumentation

The Thermo Scientific™ iCAP™ PRO XP Radial ICP-OES was chosen for the analysis. The radial instrument configuration was selected for its high matrix tolerance and reduced matrix interferences. The iCAP PRO XP ICP-OES is fully compatible with the Teledyne CETAC ASX-7400 Stirring autosampler which ensures good homogeneity of the solutions analyzed.

Method development

Reagents

The following reagents and standards were used in this work: Xylene (Fisher Scientific, Loughborough, UK); Conostan® base oil (Conostan® SCP SCIENCE, Baie- D'Urfé, Canada); S21 Conostan oil-based standard 900 mg·kg^{-1} (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn); Conostan oil-based standard 5000 mg·kg^{-1} S; Conostan oil-based standard 5000 mg·kg^{-1} Y.

The standard reference material (SRM) NIST SRM 1085c - Wear Metals in Lubricating Oil (approximate concentrations 300 mg·kg^{-1}) was analyzed as a check sample.

Sample and standard preparation

Prior to any sample or stock standard being diluted, it was homogenized by sonication. For very viscous oils, the sample can be pre-heated to 60 °C.

The yttrium oil-based standard was diluted (by weight) in xylene to give a final concentration of 10 mg·kg^{-1}. This solution was used for all dilutions, the yttrium being used as an internal standard. For all samples and standards, the final solution contained 10% oil (by weight) to ensure that differences in viscosity were minimized. To achieve this, base oil was added if required to the standards prior to dilution with the solvent.

A blank was obtained by diluting the base oil in the dilution solvent ten-fold. The standards were prepared by diluting the stock standard by weight with the dilution solvent to give the required concentration. All samples were diluted ten-fold by weight with the diluent solution.

Instrument parameters

The peristaltic pump was fitted with Solvent Flex pump tubing to introduce the sample and remove waste from the spray chamber. A concentric nebulizer was used in conjunction with a baffled spray chamber. This combination was selected because it reduces the overall amount of solvent reaching the plasma and shows good efficiency at removing large particles from the sample aerosol. The plasma was then ignited and the appropriate parameters set (see Table 1).

Table 1. Instrument parameters.

Parameter	Setting
Pump tubing	Sample Solvent Flex orange/white Drain Solvent Flex white/white
Pump speed	30 rpm
Spray chamber	Baffled glass cyclonic
Nebulizer	Glass concentric
Nebulizer gas flow	0.35 L·min^{-1}
Auxiliary gas flow	1.5 L·min^{-1}
Coolant gas flow	12 L·min^{-1}
Center tube	1 mm
RF power	1150 W
Radial viewing height	12 mm
Repeats	3
Exposure time	15 s
Uptake time	45 s
Wash time	30 s

Using the intuitive wavelength selection tool of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, wavelengths were selected that were most likely to be free from interferences in this matrix. ASTM D5185 also gives a non-exhaustive list of suggested wavelengths that can be used as a guideline. Once each of the samples and standards were analyzed the subarray plots were examined and changes were made to correct for interferences and optimize background corrections, as necessary. From the results obtained it was found that no mathematical correction factors such as Inter-Element Correction (IEC) were required. The wavelengths used for analysis and internal standard correction are shown in Table 2.

Table 2. Analytic and internal standard wavelength used as well as detection limit.

Element and wavelength (nm)	Internal standard wavelength (nm)	DL (µg·kg^{-1})
Ag 338.289	Y 324.228	6.7
Al 308.215	Y 324.228	33
Al 396.152	Y 324.228	15
B 208.959	Y 324.228	17
Ba 233.527	Y 224.228	2.1
Ca 184.006	Y 224.229	28
Cd 214.438	Y 224.230	1.2
Cr 267.716	Y 360.073	2.2
Cu 324.754	Y 324.228	2.3
Fe 238.204	Y 324.228	4.1
Mg 279.553	Y 360.073	0.3
Mo 281.615	Y 360.073	7.1
Na 589.592	Y 324.228	16
Ni 231.604	Y 324.228	10
P 178.284	Y 224.229	54
Pb 220.353	Y 224.229	30
S 180.731	Y 224.229	9.9
Si 212.412	Y 224.229	19
Sn 283.999	Y 324.228	23
Ti 334.941	Y 324.228	1.0
V 309.311	Y 324.228	1.6
Zn 213.856	Y 324.228	2.2

Analysis

Xylene was aspirated for a period of 10 minutes prior to analysis. The method ASTM D5185 calls for wavelength profiling to be carried out prior to analysis. Due to the stability and intelligent design of the iCAP PRO XP ICP-OES, this is not needed. The instrument was calibrated by running a 3 point calibration and then a check standard was run (NIST 1085c).

The measured value of the check is required to be within ±5% of the certified value for the analysis to continue, both after the initial calibration and at regular intervals every fifth sample.

Results

The results of the sample analysis can be seen in Table 3. Although the iCAP PRO XP Radial ICP-OES is capable of detecting low concentrations, as demonstrated by the results of elements such as magnesium, ASTM D5185 expects detectability in the low mg·kg^{-1} range for most elements to be sufficient. Focus is on trend analysis and identification of high concentrations of wear metals and additives in the oil/engine under study. The recovery of the check standard was better than ±5% for the 5 analyses performed (Table 3). As described in the standard method, certified standards should be regularly analyzed to verify accuracy and precision of the instrument calibration.

Table 3. Concentration results and average recovery of the certified reference material analysis.

Element and wavelength (nm)	Average concentration (n=5) (mg·kg^{-1})	Reference value (mg·kg^{-1})	Average recovery CRM 1085c
Ag	298.2	298	100.1
Al	298.4	292	102.2
Al	297.3	292	101.8
B	318.8	304	104.9
Ba	294.0	306	96.1
Ca	312.6	299	104.6
Cd	304.4	301	101.1
Cr	301.3	302	99.8
Cu	309.6	298	103.9
Fe	314.0	301	104.3
Mg	296.1	300	98.7
Mo	304.8	305	99.9
Na	305.1	300	101.7
Ni	312.9	306	102.3
P	293.3	304	96.5
Pb	301.5	303	99.5
S	313.6	-	ND
Si	305.7	293	104.3
Sn	297.0	298	99.7
Ti	298.2	300	99.4
V	299.1	285	105.0
Zn	293.3	285	102.9

*ND: not determined

Conclusion

The design of the Thermo Scientific iCAP PRO XP Radial ICP-OES enables for its high matrix tolerance which makes it ideal for such challenging analysis. High speed of analysis is accomplished by covering the whole wavelength range within just one simultaneous acquisition making the iCAP PRO XP Radial ICP-OES the perfect fit for high throughput environments. The removable and easily cleaned interface parts reduce downtime, due to maintenance, to a minimal. The system is capable of meeting the requirements of the standard method ASTM D5185 which details direct analysis of lubricating oils for wear metals and additives. Also low analysis time per sample is achieved with the iCAP PRO Series ICP-OES, which is often a requirement for analyzing used oil samples in laboratories facing both a high volume of samples and the constraint for fast turnaround analysis times. Time is undeniably a key factor in preventative maintenance and reducing downtime costs.

Find out more at **thermofisher.com/ICP-OES**

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