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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 costs incurred by unscheduled maintenance of engines and machinery can be very high in both labor and materials, as well as the profits lost due to equipment downtime. As such, the analysis of wear metals, contaminants and additive elements in lubrication oils is a valuable diagnostic tool to allow for the accurate scheduling of preventative maintenance to equipment. The high temperature source of an ICP-OES, with its ability to dissociate any organometallic compounds and handle difficult organic solvent matrices, makes analysis by 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 sample digestions, 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 and it should also be highlighted that, in this case, obtaining a representative sample would be very difficult.

Instrumentation

The Thermo Scientific™ iCAP™ PRO XP Radial ICP-OES was chosen for the analysis, as the radial view provides high matrix tolerance with reduced matrix interferences. In order to maintain good sample homogeneity during analysis, a Teledyne CETAC ASX-7400 Stirring autosampler was connected to the iCAP PRO XP ICP-OES with full control integrated into the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Method development

Reagents

The following reagents and standards were used in this work: CONOSTAN PremiSOLV ICP Solvent; CONOSTAN base oil; S21 CONOSTAN oil-based standard 900 $mg \cdot kg^{-1}$ (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 $mg \cdot kg^{-1}$ S; CONOSTAN oil-based standard 5000 $mg \cdot kg^{-1}$ Y.

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

Sample and standard preparation

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

In order to produce dilutions, standards (and samples as required) were diluted with base oil, maintaining the sample matrix. The yttrium oil-based standard was added to the PremiSOLV diluent to give an approximate concentration of 10 $mg \cdot kg^{-1}$. This diluent was then used to dilute all samples and standards by a factor of 1:10 (weight:weight), which minimizes differences in sample viscosity and allows yttrium to be used as an internal standard. The exact weights of standards, base oil and diluent can then either be recorded accurately and programmed into the analysis sample list, or all weights can be taken within an acceptance tolerance (commonly ±0.5%).

Instrument parameters

Solventflex peristaltic pump tubing was used to introduce the sample and remove waste from the spray chamber as it is resistant to organic solvents, providing a long lifetime. The iCAP PRO radial organic sample introduction kit was used to reduce the amount of solvent entering the plasma. Additionaly, a ceramic D-torch was used as this torch minimizes the required maintenance frequency. Details of the sample introduction setup and applied instrument's plasma settings can be found in Table 1.

Table 1. Instrument parameters

Parameter	Setting
Pump tubing	Sample SolventFlex orange/white Drain SolventFlex white/white
Pump speed	40 rpm
Spray chamber	Baffled glass cyclonic
Nebulizer	Glass V-Groove
Nebulizer gas flow	0.40 $L \cdot min^{-1}$
Auxiliary gas flow	1.5 $L \cdot min^{-1}$
Coolant gas flow	12.5 $L \cdot min^{-1}$
Center tube	1 mm
RF power	1250 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 Qtegra 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. The calibration standards and a selection of samples were analyzed so that the subarray plots could be examined in order to optimize peak and background integration areas and correct for any interferences. From the results obtained, it was found that no mathematical correction factors such as Inter-Element Correction (IEC) were required. The yttrium emission line at 371.030 nm was used for monitoring the internal standard, and the analytical wavelengths used for the analyses are shown in Table 2.

Analysis

Once the plasma was lit, the Qtegra ISDS Software Get Ready function was configured to aspirated PremiSOLV for 10 minutes to allow both the plasma and optic purge to stabilize. After this time, the instrument was then ready for analysis. The method ASTM D5185 calls for wavelength profiling to be carried out prior to analysis; however, 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 calibration verifcation was performed using a check standard (NIST 1085c).

Table 2. Analytical wavelengths, concentration average, recovery and precision of the certified reference material analysis

Element	Wavelength (nm)	Average concentration (n=10) ($mg \cdot kg^{-1}$)	Relative standrad deviation (n=10) (%)	Reference value ($mg \cdot kg^{-1}$)	Average recovery CRM 1085c (%)
Ag	328.068	289.9	0.2	298	97.3
Al	396.152	297.5	0.1	292	101.9
B	208.959	294.4	0.8	304	96.9
Ba	233.527	294.2	0.2	306	96.1
Ca	315.887	306.6	0.2	299	102.6
Cd	214.438	311.2	0.4	301	103.4
Cr	267.716	303.5	0.2	302	100.5
Cu	324.754	302.1	0.2	298	101.4
Fe	259.940	314.5	0.2	301	104.5
Mg	285.213	295.6	0.1	300	98.5
Mn	293.930	310.5	0.1	299	103.9
Mo	202.030	304.4	0.2	305	99.8
Na	589.592	303.6	0.2	300	101.2
Ni	231.604	314.9	0.3	306	102.9
P	178.284	298.7	0.4	304	98.2
Pb	220.353	302.7	0.5	303	99.9
S	180.731	8939.4	0.4	N/A	N/A
Si	212.412	305.1	0.2	293	104.1
Sn	283.999	296.2	0.2	298	99.4
Ti	334.941	299.4	0.1	300	99.8
V	309.311	295.7	0.1	285	103.8
Zn	206.200	295.3	0.4	285	103.6

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 (Initial Calibration Verfication - ICV) and at regular intervals every fifth sample (Continuing Calibration Verification - CCV).

In order to measure the method's precision, this CRM sample was prepared and analyzed ten times.

Results

The results of the sample analysis can be seen in Table 2. While the iCAP PRO XP Radial ICP-OES is capable of detecting low concentrations (sub mg·kg^{-1}), the focus of the analysis is on the identification of high concentrations and trending of wear metals and additives in the oil/engine under study; therefore, ASTM D5185 expects detectability in the low mg·kg^{-1} range for most elements to be sufficient. As can be seen in Table 2, the mean recovery of the check standard was better than ±5% for all 10 analyses performed and the precision, measured as relative standard deviation (%) for all elements, was below 1%.

Sample throughput

In most used lubrication oil labs, the number of samples requiring analysis can easily be in the 1000s per day, so very high productivity is essential. In order to improve analysis throughput, two factors must be considered: the analysis time per sample and the amount of time the instrument is performing sample analysis, commonly known as instrument uptime.

Speed of analysis

A breakdown of the sample analysis stages in this method can be seen in Table 3. Using these values, it is apparent that the iCAP PRO XP radial ICP-OES provides a sample analysis time of 67 seconds per sample*. For very high throughput facilities, it is common to reduce the number of analytical repeats to 2. When combined with an optimal instrument and autosampler layout, analysis time can be reduced even further.

Instrument uptime

A laboratory's throughput of samples is reduced anytime the instrument is not performing analysis. This includes the plasma warm up, stabilization time and time spent cleaning and maintaining the instrument. The efficient optic tank design and RF generator of the iCAP PRO ICP-OES only requires a 5-minute stabilization time (following ignition) before analysis can occur**, which means sample analysis can start very rapidly.

During the analysis of oil samples, the main causes of maintenance are: carbon soot formation in the plasma and subsequent deposition on torch components and interface surfaces, matrix deposits in the nebulizer and matrix deposits on interface optic surfaces. During daily analysis, any of these effects will require analysis to be stopped and timely cleaning to be performed. The instrument must then be re-calibrated before sample analysis can resume.

To prevent unscheduled maintenance from these sources, the iCAP PRO Series ICP-OES features a number of options. The system is compatible with a ceramic D-torch, which prevents torch de-vitrification and provides a very long lifetime with minimum deposit cleaning. In order to prevent carbon soot deposits, the iCAP PRO XP Radial ICP-OES comes with an additional gas line as standard that can easily be supplied with clean synthetic air or pure oxygen. Flowing just 50–100 µl/min of either of these gases into the plasma converts the carbon soot into carbon dioxide, reducing or eliminating the need for cleaning carbon deposits, depending on the carbon load.

To minimize the downtime required for maintenance procedures, the iCAP PRO Series ICP-OES features an easily demountable outer torch box for quick removal and cleaning, and an easily accessible sealed optics window, which protects the instrument's fore and main optics from wear that can be removed easily without tools in a matter of minutes to be rapidly cleaned as required.

*For extremely high throughput requirements, analysis times can be further reduced with the Thermo Scientific™ iCAP™ PRO XPS ICP-OES.

**Requires continual flow of purge gas during instrument shutdown.

Table 3. Timing Breakdown of the various stages of a single analysis and resulting Speed of Analysisfor the iCAP PRO XP ICP-OES

Fast uptake pump speed	Uptake time	Stabilization delay	Integration time	Repeats	Wash time	Total analysis time per sample
100 rpm	15 s	5 s	5 s	3	20 s	67 s

Conclusion

The design of the Thermo Scientific iCAP PRO XP Radial ICP-OES provides high matrix tolerance with rapid analysis times, making it ideal for the challenging high-throughput analysis of lubrication oils. The easily removed and cleaned interface and sample introduction components keep maintenance downtime to a minimum. Additionally, the use of an integrated air or oxygen additional gas will further limit maintenance requirements. The system is more than capable of meeting the analysis requirements of the standard method ASTM D5185, which details direct analysis of lubricating oils for wear metals and additives. The method described has a rapid sample analysis time of 67 seconds per sample; however, should higher throughput be required, this time can be further reduced as described in the *Speed of analysis* section.

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