Sprint analysis of lubricating oils using the Thermo Scientific iCAP 7600 ICP-OES

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Key Words
High throughput, Lubricating oil, Sprint valve, Used oil, Wear metals

Goal

This application note describes how the Thermo Scientific™ iCAP™ 7600 ICP-OES Radial and its integrated sampling valve offer high throughput capabilities to laboratories analysing lubricating oil samples. The instrument combines fast analysis time with excellent analytical performance for superior productivity and reduced cost of analysis.

Introduction

The analysis of lubricating oils is a powerful tool in preventative maintenance of engines and machinery. Regular oil sampling and trend analysis will give precious information about the state of a motor, gear transmission or mechanical part, and signify the need for maintenance before critical failures. In particular, elemental analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is used to determine the concentration of wear metals, contaminants and additives present in used oils that can be sampled from car to train fleets, or even large construction or mining machines. Wear metals are elements such as Fe, Cu and Ni, and their presence may indicate wear of metallic parts. Other elements may give evidence of contamination from foreign matter, for example Si and dirt entering the engine via a faulty filter. Additives which are typically Ca, P or Zn based compounds are added artificially to the oil to improve lubricating properties. Monitoring the depletion of these elements may therefore help in identifying optimum conditions and maintenance scheduling.

Preventative maintenance means less downtime on the equipment thereby reducing the need for expensive repairs. The result is that specialist laboratories performing this type of analysis face the challenges of both a high volume of samples and fast turnaround requirements. Lubricating oil analysis by ICP-OES is an established method with a typical analysis time for the determination of more than twenty elements of around one to two minutes per sample. This work describes how coupling an innovative sample introduction system to powerful instrumentation enables analysis time to be reduced significantly while retaining the analytical requirement of the industry. In turn, this allows rapid decisions to be taken and imminent mechanical failure to be identified.

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Instrumentation

The Thermo Scientific iCAP 7600 ICP-OES Radial was chosen for the analysis. The instrument configuration combines the enhanced matrix tolerance of the dedicated radial plasma view with high throughput capabilities of the integrated Sprint valve. The sampling valve helps to reduce flush and rinse time during analysis, thereby decreasing total analysis time significantly. It uses a vacuum pump, the traditional ICP-OES peristaltic pump and a 6-port valve fitted with a sample loop. When the valve is in the load position, the vacuum pump fills the sample loop in a few seconds while the rinse solution is pumped through the nebulizer by the peristaltic pump. When the position switches to inject, the sample is pushed into the nebulizer for analysis via the carrier/rinse solution by the peristaltic pump. At the same time, the autosampler probe is moved to the rinse station and flushed with rinse solution using the vacuum pump. This system enables a reduction of sample uptake times to mere seconds.

The iCAP 7600 ICP-OES is compatible with the CETAC ASX-1400 stirring autosampler which ensures homogeneity of the solutions analyzed. The use of the CETAC APS-1650 Automated Prep Station is also recommended for this type of analysis as it reduces sample preparation time, typically the limiting step of high throughput analysis. In this case, dilutions are made on a volume to volume basis.

Method

Reagents

The following standards were used in this work: Element Blank Oil 75, Conostan® (SCP SCIENCE, Baie-D'Urfé, Canada); 21-Element Oil Standard 500 mg/kg containing Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn, SPEX CertiPrep® (SPEX CertiPrep Group, Metuchen, US); a higher-concentration standard 5000 mg/kg for the additive elements (Ba, Ca, Mg, P, Zn), AM-Special custom blend, Conostan; oil-based standard 5000 mg/kg S and oil-based standard 5000 mg/kg Y, Conostan. General purpose white spirit was used as a solvent.

Sample and standard preparation

For all elements except S, standards at 50, 100, 250 and 500 mg/kg were prepared, plus standards at 1000, 2500 and 5000 mg/kg for Ba, Ca, Mg, P and Zn. Separate standards were also prepared at 2500 and 5000 mg/kg for S. Y was used as an internal standard and added to the white spirit to obtain a 20 mg/L Y solution used for all further dilutions. All samples and standards were therefore diluted 1:10 (w/v) with the later.

By ensuring that the final solution always contains 10% oil (weight or volume), differences in viscosity are minimized; therefore, when required, base oil is added to the standard or sample prior to the addition of the diluent. Furthermore, oil analysis is usually expressed directly in ppm or mg/kg in the oil sample, the solvent dilution being negligible. All concentrations in this work are therefore expressed in sample terms (including calibration standards).

Instrument and method parameters

The Sprint valve of the Thermo Scientific iCAP 7600 ICP-OES was used for this analysis in conjunction with the Sprint analysis mode to enable extremely fast analysis times. The standard organic sample introduction kit was also fitted to the instrument. It comprises a V-groove nebulizer, a baffled spray chamber and a 1 mm centre tube. All parameters used for the analysis including settings of the Sprint valve are listed in Table 1 and Figure 1. When using the sampling valve, flush and rinse behaviors are driven by the valve settings. There is no need therefore for faster flush pump speed or wash time to be set as in traditional methods. The flush pump rate is identical to the analysis pump speed (no pump stabilization time required) and the wash time in the method is set to zero.

Table 1. Parameters used for analysis

Instrument parameters	
Inlet pump tubing	Solvent Flex (1.016 mm)
Outlet pump tubing	Solvent Flex (1.524 mm)
Loop size	1.02 mL
Pump speed	40 rpm
Uptake time	12 sec
Nebulizer	V-groove
Spray chamber	Baffled cyclonic
Centre tube	1 mm
Torch	EMT
Plasma parameters	
RF power	1350 W
Nebulizer gas flow	0.4 L/min
Auxiliary gas flow	1.5 L/min
Coolant gas flow	14 L/min
Radial viewing height	12 mm
Analysis parameters	
Analysis mode	Sprint
Exposure time	1 sec
Repeats	2

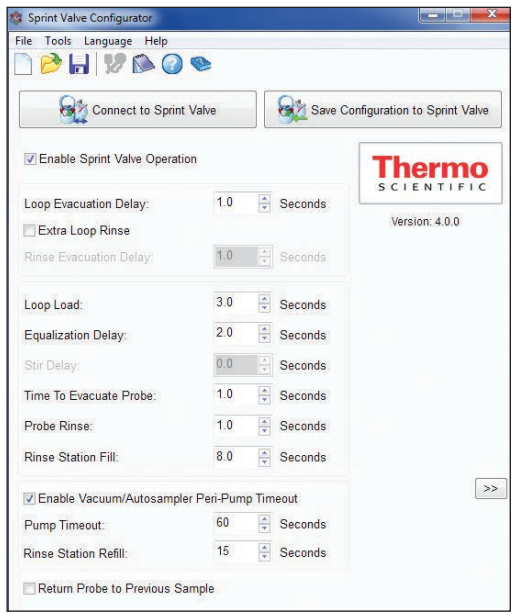

Figure 1. Sprint valve settings

Method development

Using the intuitive wavelength selection tool of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS), wavelengths were selected that were most likely to be free from interferences in this matrix (Figure 2).

Figure 2. Intuitive wavelength selection of Qtegra ISDS

Typically, concentrations ranging from single ppm level for wear metals, up to thousands of ppm for additive elements are expected in lubricating oils. Wavelengths were therefore also chosen following these criteria to achieve the required detection limits for wear metals and linearity for additives. Selected wavelengths are listed in Table 2. Ba and Mg are considered as additive elements, but they are not used as widely as Ca, P and Zn based compounds, hence their concentration can vary significantly in oils. A combination of two wavelengths for these elements was kept with switching from Mg 279.079 nm to Mg 277.669 nm and Ba 233.527 nm to Ba 234.758 nm above 500 mg/kg to extend linearity of the method if required. A similar approach could be taken for Ca and Zn. In this work, linear calibrations (see details in Table 2) were obtained with coefficients of correlation better than 0.9995 for all elements.
Y 224.306 nm and 242.220 nm were chosen for internal standard correction.

Table 2. Wavelengths, calibration standards and detection limits (DL) of the optimised method

Wavelength	Calibration standards (mg/kg)	DL (mg/kg)*	Comments
Ag 328.068 nm	0, 100, 250	0.5	
Al 309.271 nm	0, 100, 250, 500	2	No right background point (V)
B 208.959 nm	0, 100, 250, 500	2	
Ba 233.527 nm	0, 100, 250, 500	1	
Ba 234.758 nm	0, 250, 500, 2500, 5000	5	
Ca 220.861 nm	0, 250, 500, 2500, 5000	50	Estimated linearity > 15000 ppm
Cd 214.438 nm	0, 100, 250	0.2	
Cr 205.560 nm	0, 100, 250, 500	0.5	
Cu 224.700 nm	0, 100, 250, 500	1	
Fe 261.187 nm	0, 100, 250, 500	1	
Mg 277.669 nm	0, 250, 500, 2500, 5000	25	
Mg 279.079 nm	0, 100, 250, 500	5	
Mn 293.306 nm	0, 100, 250	0.5	
Mo 281.615 nm	0, 100, 250, 500	0.5	
Na 589.592 nm	0, 100, 250	0.5	
Ni 230.300 nm	0, 100, 250, 500	0.5	
P 185.942 nm	0, 250, 500, 2500, 5000	5	
Pb 220.353 nm	0, 100, 250, 500	2	
S 182.624 nm	0, 2500, 5000	50	Estimated linearity > 15000 ppm
Si 251.611 nm	0, 100, 250, 500	1	
Sn 283.999 nm	0, 100, 250, 500	5	
Ti 339.458 nm	0, 100, 250, 500	1	
V 268.796 nm	0, 100, 250, 500	1	
Zn 330.259 nm	0, 250, 500, 2500, 5000	10	No right background point (Zn)

*DL estimated as three times the standard deviation (SD) calculated over 10 blanks

Analysis and results

Two typical oil samples (Oil A and Oil B) were analyzed following the *Sprint* method described previously. The results are shown in Table 3. They were compared to the concentrations obtained for the same oils analyzed with a traditional method. The Speed analysis was performed using the instrument peristaltic pump in a conventional way (no Sprint valve). *Speed* analysis mode was selected with five seconds integration time and two replicates. Analytical wavelengths were optimized for the method and may be different than defined for the *Sprint* analysis.

Table 3. Results (mg/kg) obtained for Oil A and Oil B with *Sprint* and *Speed* methods

Element	Oil A		Oil B	
	Sprint	*Speed*	*Sprint*	*Speed*
Ag	< 0.5	< 0.1	< 0.5	< 0.1
Al	2.1	1.9	8.9	9.6
B	< 2	0.8	< 2	1.3
Ba	< 1	0.2	3.0	3.2
Ca	2740	2830	17330	17750
Cd	< 0.2	< 0.05	< 0.2	< 0.05
Cr	0.9	0.8	0.8	0.7
Cu	1.3	1.6	1.7	1.6
Fe	20.6	20.6	30.6	29.3
Mg	248	246	41	41
Mn	0.6	0.6	5.0	5.3
Mo	4.3	4.4	1.1	0.8
Na	7.0	7.0	87	84
Ni	< 0.5	0.3	67	70
P	1040	1060	360	369
Pb	< 2	1.0	< 2	< 0.5
S	8180	7670	15010	14030
Si	4.2	4.3	20.0	18.9
Sn	< 5	< 1	< 5	< 1
Ti	< 1	< 0.2	1.5	0.6
V	< 1	< 0.2	62	66
Zn	1220	1240	419	419

Comparison within the two methods was found to be good with relative standard deviation (RSD) below 5% for elements present at significant concentrations in Oil A and Oil B. Although detection limits for this *Speed* method are estimated to be five times lower then for the *Sprint* method, this is below the industry requirement which is typically around the single ppm level. The *Sprint* analysis was noticeably faster with 27 seconds analysis time per sample compared to approximately three times longer for samples analyzed with the *Speed* method.

Accuracy of the *Sprint* method is also shown in Table 4 with recoveries obtained for a check standard prepared at 50 mg/kg (all elements except additives and S). Recoveries were good with bias below 5% for all elements except B (within 10%).

Table 4. Results obtained for a 50 mg/kg check standard

Element	Measured conc. (mg/kg)	Recovery (%)
Ag	49.9	99.8
Al	50.3	100.6
B	46.5	93.1
Ba	52.4	104.8
Cd	49.4	98.8
Cr	49.5	99.0
Cu	49.2	98.3
Fe	50.5	101.0
Mg	49.2	98.5
Mn	49.6	99.2
Mo	50.3	100.6
Na	50.1	100.1
Ni	49.2	98.5
Pb	50.0	100.0
Si	50.1	100.2
Sn	52.3	104.5
Ti	50.7	101.5
V	50.2	100.5

Excellent stability of the *Sprint* analysis was demonstrated by measuring check standards every half an hour over a four hour period (100 mg/kg for wear metals and 1000 mg/kg for additives). Recoveries are shown in Figure 3. Recoveries for all elements over the four hour analysis were well within 10% of the expected concentrations with most elements within 5%. Overall RSD on the measurements were also found to be good and below 2% for all wavelengths. No re-calibration was required although this could be automatically set-up within Qtegra ISDS, as a comprehensive choice of actions related to QC or check standards is available for selection from the software.

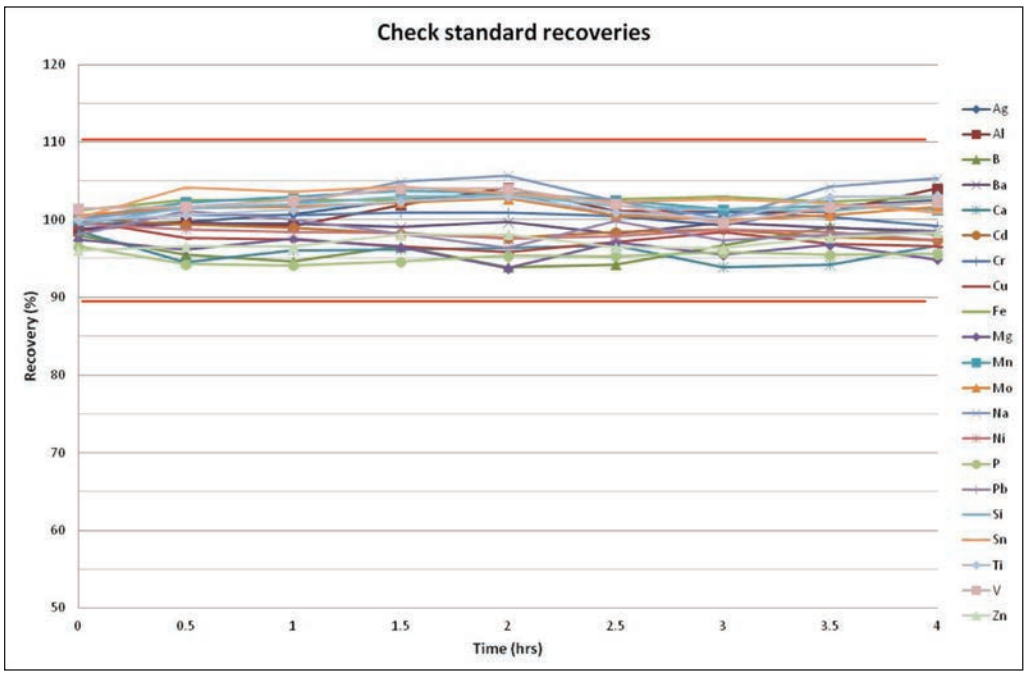

Figure 3. Stability over a four hour period for wear metals and additives

Conclusion

The Thermo Scientific iCAP 7600 ICP-OES Radial was successfully used for high throughput lubricating oil analysis. The intelligent design of the sample introduction system with an integrated sampling valve allows analysis time per sample below 30 seconds. Analytical performance was also demonstrated giving accuracy, precision and stability for hundreds of samples, reducing the number of QC, re-calibrations and samples to be re-analyzed, but also reducing costs of analysis per sample. The iCAP 7600 ICP-OES instrument offers superior capacity of analysis for laboratories seeking optimum productivity.

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