Multi-Element Analysis of Fuel and Lubricating Oils by Simultaneous ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

The determination of metal levels in both fuel oil and lubricating oils is of prime importance to the industrial machinery, transport and utility industries. In general, metal levels are determined to provide early warning of failure of components in physical contact with the oil. Oil analysis can also indicate whether oil in a system has been contaminated by another source, other than wear. For example increases in silicon or aluminum levels may indicate dirt contamination or increased levels of sodium, perhaps seawater contamination or antifreeze leakage [1]. Conversely, a decrease in the levels of additive metals (for example, Ca, Mg, Zn, Pb) may indicate a dilution of the oil by one oil not containing these additives. Many large fleet operators and mining companies rely on the analysis of used lubricating oil samples to extend the period between oil changes in their equipment and to warn of the beginning of mechanical failure so that preventive maintenance may be scheduled.

In this study various fuel oils and National Institute of Standards and Technology (N.I.S.T.), standard reference material (S.R.M.) 1084a Wear Metals in Lubricating Oil, were diluted in dekalin (decahydronaphthalene) and analyzed using a Agilent Vista simultaneous Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-OES) with the axially viewed plasma.

Agilent Technologies

For the analysis of volatile organic solvents with an axially viewed ICP, the Auxiliary Gas Module 1 (AGM-1) oxygen accessory is required. The AGM-1 adds a small flow of oxygen to the plasma auxiliary gas, thus reducing molecular band emissions. This gives lower detection limits, and prevents the build up of carbon within the torch and on the cooled cone interface.

The use of a simultaneous ICP-OES instrument significantly improves the efficiency of analysis when a large number of elemental determinations are to be made. Typically, large laboratories specializing in used oil analysis test hundreds of samples each day. In this study 21 elements were determined at around 105 seconds per sample including sample introduction and rinse time. It should be noted that the measurement of more than this number of elements would not add further to the analysis time due to the simultaneous detection of the Vista.

Instrumental

The Vista simultaneous ICP-OES with axially viewed plasma was used for the analysis. The Vista features a free running, air-cooled, 40 MHz RF generator and cooled cone interface. The Vista's optical system is based on an echelle polychromator with CCD detector [2]. The polychromator is thermostatted to 35 °C for stability and the unique CCD detector features 70,000 pixels (detectors) arranged to exactly match the 2 dimensional echellogram. The detector provides rapid readout and excellent detection limits. The instrument was controlled with an IBM computer with an Intel Pentium processor and Agilent's Vista software running under Microsoft Windows NT operating system.

In this work, a Vista with manual gas pressure regulator was used. Mass flow control of the nebulizer flow, which allows the nebulizer gas flow to be automatically adjusted, is available as an option.

Instrument parameters

Power	1.3 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	0.75 L/min
Nebulizer type	Glass concentric type K
Torch type	Demountable with 1.8 mm quartz injector
Spray chamber type	Sturman-Masters
Pump speed	15 rpm
Pump tubing	Inlet:–viton, black/black (0.76 mm id), Outlet:–viton, white/white (1.02 mm id)
Sample uptake rate	0.6 mL/min
AGM – 1 setting	5 (130 mL/min)
Sample delay	15 seconds
Stabilization time	45 seconds
Fast pump	On
Replicate time	5 seconds
Replicates	3
Background correction	Off peak background correction or fitted back ground correction. Fast Automated Curve Fitting Technique (FACT) was used for Na 588.995 nm

Sample Preparation

Approximately 2 g of used oil was accurately weighed into a 20 mL volumetric flask and made up to volume with dekalin.

One gram of N.I.S.T, S.R.M 1084a Wear Metals in Lubricating Oil was accurately weighed into a 50 mL volumetric flask and made up to volume with dekalin.

Results

In this study seven fuel oil samples and one lubricating oil sample were analyzed. The lubricating oil was a standard reference material obtained from NIST, Gaithersburg, MD, USA and used to validate the method. Triplicate analyses were performed and the average result is shown.

Table 1.

	Ag 328.068 nm	Al 257.509 nm	B 249.678 nm	Ba 493.408 nm	Ca 317.933 nm	Cd 226.502 nm
IC 1 (mg/kg)	0.011 ± 0.002	5.83 ± 0.03	< 0.2	< 0.003	5.35 ± 0.06	< 0.02
IC 2 (mg/kg)	0.0148 ± 0.0005	28.7 ± 0.1	< 0.2	< 0.003	26.5 ± 0.3	< 0.02
IC 3 (mg/kg)	0.04 ± 0.01	114.6 ± 1.3	0.270 ± 0.01	< 0.003	109.0 ± 0.6	< 0.02
IC 5/4 (mg/kg)	0.04 ± 0.01	2.80 ± 0.03	< 0.2	37.5 ± 0.3	222 ± 1	0.95±0.02
IC 6 (mg/kg)	0.09 ± 0.01	< 1	1.34 ± 0.1	< 0.003	640 ± 4	< 0.02
IC 10 (mg/kg)	0.031 ± 0.002	< 1	0.53 ± 0.08	16.3 ± 0.2	3210 ± 7	0.117 ± 0.003
IC 15 (mg/kg)	< 0.01	< 1	< 0.2	< 0.003	0.974 ± 002	< 0.02
N.I.S.T S.R.M 1084a	100.3 ± 1.2	100.4 ± 0.4	–	–	–	–
Certified value (mg/kg)	101.4 ± 1.5	(104)	–	–	–	–

< Values expressed as 10 times the standard deviation of background emission
Values in parenthesis are not certified but provided for information only.
—- Value not certified.

Table 2:

	Cr 267.716 nm	Cu 324.754 nm	Fe 259.940 nm	Mg 279.553 nm	Mo 284.824 nm	Mn 257.610 nm
IC 1 (mg/kg)	6.21 ± 0.05	6.41 ± 0.04	5.95 ± 0.05	0.067 ± 0.007	< 0.1	5.69 ± 0.03
IC 2 (mg/kg)	29.4 ± 0.3	29.3 ± 0.1	28.5 ± 0.4	0.16 ± 0.03	< 0.1	28.2 ± 0.3
IC 3 (mg/kg)	113.9 ± 0.7	115.1 ± 0.5	112.8 ± 0.8	0.19 ± 0.04	< 0.1	107.4 ± 0.5
IC 5/4 (mg/kg)	3.05 ± 0.05	22.8 ± 0.3	50.9 ± 0.7	2.04 ± 0.05	< 0.1	0.958 ± 0.009
IC 6 (mg/kg)	< 0.02	0.16 ± 0.03	1.11 ± 0.02	69.9 ± 0.9	21.4 ± 0.4	0.161 ± 0.002
IC 10 (mg/kg)	0.131 ± 0.002	1.32 ± 0.02	6.5 ± 0.1	10.5 ± 0.2	0.46 ± 0.01	0.233 ± 0.003
IC 15 (mg/kg)	< 0.02	0.17 ± 0.01	0.44 ± 0.05	0.310 ± 0.005	< 0.1	0.006 ± 0.002
N.I.S.T S.R.M 1084a	96.8 ± 1.3	97.6 ± 1.1	98.8 ± 2.4	97.9 ± 1.5	98.8 ± 1.5	—-
Certified value (mg/kg)	98.3 ± 0.8	100.0 ± 1.9	98.9 ± 1.4	99.5 ± 1.7	100.3 ± 1.4	—-

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—- Value not certified

Table 3.

	Na 588.995 nm	Ni 216.555 nm	P 213.618 nm	Pb 220.353 nm	Si 251.611 nm	Ti 334.941 nm
IC 1 (mg/kg)	0.436 ± 0.006	5.80 ± 0.03	< 1	0.98 ± 0.02	6.01 ± 0.08	5.45 ± 0.03
IC 2 (mg/kg)	2.24 ± 0.05	28.3 ± 0.2	< 1	2.5 ± 0.2	29.4 ± 0.2	29.1 ± 0.2
IC 3 (mg/kg)	2.97 ± 0.06	108 ± 1	< 1	48.1 ± 0.7	112.7 ± 0.7	112.7 ± 0.7
IC 5/4 (mg/kg)	6.7 ± 0.1	< 0.1	119.5 ± 0.7	19.1 ± 0.2	7.57 ± 0.09	0.205 ± 0.008
IC 6 (mg/kg)	0.62 ± 0.01	< 0.1	248 ± 3	< 0.3	1.58 ± 0.03	0.011 ± 0.004
IC 10 (mg/kg)	37.1 ± 0.8	3.08 ± 0.03	237 ± 5	0.91 ± 0.02	2.78 ± 0.03	0.064 ± 0.004
IC 15 (mg/kg)	4.82 ± 0.05	4.58 ± 0.08	< 1	< 0.3	< 0.5	< 0.01
N.I.S.T S.R.M 1084a	—-	100.2 ± 1.2	—-	100.0 ± 0.9	96.1±0.9	98.9 ± 1.3
Certified value (mg/kg)	—-	99.7 ± 1.6	—-	101.1 ± 1.3	(103)	100.4 ± 3.8

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Table 4:

	V 311.070 nm	Zn 213.857 nm
IC 1 (mg/kg)	5.68 ± 0.03	5.76 ± 0.05
IC 2 (mg/kg)	28.3 ± 0.3	28.2 ± 0.3
IC 3 (mg/kg)	112 ± 2	108.1 ± 0.7
IC 5/4 (mg/kg)	< 0.1	32.4 ± 0.5
IC 6 (mg/kg)	< 0.1	250 ± 2
IC 10 (mg/kg)	5.91 ± 0.06	238 ± 2
IC 15 (mg/kg)	15.3 ± 0.2	0.356 ± 0.007
N.I.S.T S.R.M 1084a	96.4±1.3	—-
Certified value (mg/kg)	95.9 ± 9.4	—-

< Values expressed as 10 times the standard deviation of background emission
—- Value not certified

Discussion

For the NIST SRM 1084a sample, measured values are in good agreement with the certified values demonstrating the suitability of the axial Vista ICP-OES for the analysis of used oils.

Background structure, the result of using an organic solvent, posed some difficulties in the measurement of sodium at 588.995 nm. Using Vista's Fast Automated Curve-fitting Technique (FACT) improved the background measurement at this line and improved the levels of detection. FACT uses Gaussian curve modeling techniques to accurately characterize and correct for neighboring spectral background [3]. FACT has been proven to provide accurate background correction even when peaks are as close as 0.2 pixels and is ideal for correcting the background observed from organic solvents.

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