AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-184, Rev. 0

SPECTRO **GENESIS**

Analysis of Lubricating Oils Using ICP-OES with Dual-Side-On Interface Plasma Observation

Introduction

The elemental analysis of oils is important for new and used lubricating oils. Wear metals in lubricating oils, such as aluminum, copper, nickel or iron can indicate wear of any oil-wetted component and if the level of wear is critical. Other elements like silicon, magnesium or potassium indicate contamination of the oil. The correct addition of elements, such as molybdenum, calcium, barium, phosphorus and zinc must be monitored. The precision of the analytical results is critical in these cases. Inductively coupled plasma optical emission spectrometry (ICP-OES) due to its multi element capability, large dynamic linear range, stability and low detection limits is accepted and/or suggested in several standard procedures for the analysis of oils [1-10].

Instrumentation

All measurements were performed with the SPECTRO GENESIS ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with dual side-on plasma observation. It enables an average factor 2 enhanced sensitivity compared to single radial plasma observation, while eliminating typical axial view interferences. In addition, it offers a high matrix compatibility, linear dynamic range and precision without the need to change the plasma observation mode during analysis. The SPECTRO GENESIS features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 175 and 770 nm can be analyzed, allowing complete spectrum capture. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time.

For UV access (<200 nm), the optical system can be purged with argon. The purge rate during normal operation is 0.5 L/min.

An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions.

For sample introduction, a Noordermeer nebulizer and a cyclonic spray chamber were used. The ICP operating conditions are given in Table 1.

Table 1: Typical ICP operating conditions

Power	1200 W
Observation mode	Dual-Side-On
Coolant flow	15.0 L/min
Auxiliary flow	2.0 L/min
Nebulizer flow	0.75 L/min
Plasma torch	Quartz, fixed, 1.8 mm injector tube
Spray chamber	Cyclonic
Nebulizer	Noordermeer
Sample aspiration rate	2 mL/min
Replicate read time	22 s per replicate

Sample Preparation

Oil standards (Conostan) and samples were diluted at room temperature to 3g using base oil 75 (Conostan) and then further diluted to 10g with kerosene (Merck). The dilution is necessary to compensate for physical properties differences of the samples.

Calibration

The concentrations of the calibration solutions are given in table 2.

Table 2: Calibration standards

Element	Std.1 [mg/kg]	Std.2 [mg/kg]	Std.3 [mg/kg]	Std.4 [mg/kg]
Ag	0	1	5	10
Al	0	1	5	10
Ba	0	1	5	10
Ca	0	1	5	10
Cd	0	1	5	10
Cr	0	1	5	10
Cu	0	1	5	10
Fe	0	1	5	10
K	0	1	5	10
Mg	0	1	5	10
Mn	0	1	5	10
Mo	0	1	5	10
Na	0	1	5	10
Ni	0	1	5	10
P	0	1	5	10
Pb	0	1	5	10
Si	0	1	5	10
Sn	0	1	5	10
Ti	0	1	5	10
V	0	1	5	10
Zn	0	1	5	10

Results and Discussion

Table 3 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [11]:

$$\mathbf{LOD = 3\ RSD_b\ c/\ 100\ SBR}$$

Where:

RSD_b: - relative standard deviation of 10 replicates of the blank (in %)

c: - concentration of the standard

SBR: - signal to background ratio

Table 3: Typical Limits of Detection (LOD) in the diluted sample for the selected lines

Element	λ [nm]	LOD (3σ) [µg/L]	Element	λ [nm]	LOD (3σ) [µg/L]
Ag	328.068	3.0	Mn	257.611	0.4
Al	308.215	23.0	Mo	202.095	3.2
B	249.773	3.1	Na	588.995	24.0
Ba	455.404	0.4	Ni	221.648	4.4
Ca	393.366	0.2	P	177.495	14.0
Cd	226.502	1.3	Pb	220.353	24.0
Cr	267.716	2.5	Si	251.612	6.6
Cu	324.754	2.4	Sn	189.991	11.0
Fe	259.941	2.0	Ti	334.941	0.9
K	766.491	90.0	V	311.071	2.1
Li	670.78	5.6	Zn	213.856	1.3
Mg	279.553	0.1			

Accuracy

The accuracy of the calibration curve was confirmed by the analysis of a QC Standard (2 mg/kg). Comparison of the measured results (table 4) shows excellent agreement with the given values. The precision for 10 replicates measurements ranged from 0.4 to 0.7% RSD.

Table 4: Result of the QC-Standard

Element/Line	Measured Concentrations [mg/kg]	Given Concentrations [mg/kg]	Recovery [%]
Ag	1.98	1.963	100.9
Al	1.98	1.963	100.9
B	2.03	1.963	103.4
Ba	1.99	1.963	101.4
Ca	2.02	1.963	102.9
Cd	1.98	1.963	100.9
Cr	1.99	1.963	101.4
Cu	1.99	1.963	101.4
Fe	2.01	1.963	102.4
K	1.94	1.963	98.8
Li	1.98	1.963	100.9
Mg	2.02	1.963	102.9
Mn	2.01	1.963	102.4
Mo	1.99	1.963	101.4
Na	1.98	1.963	100.9
Ni	2.00	1.963	101.9
P	1.97	1.963	100.4
Pb	2.02	1.963	102.9
Si	1.99	1.963	101.4
Sn	1.99	1.963	101.4
Ti	1.99	1.963	101.4
V	2.00	1.963	101.9
Zn	2.00	1.963	101.9

Conclusion

The SPECTRO Genesis with dual-side-on interface offers a fast, accurate and precise method for the simultaneous determination of trace elements, wear metals and additives in lubricating oils. Even though the sensitivity gain in an organic matrix is not as big as in an aqueous matrix, still, using the DSOI interface results in an average improvement factor of 1.5 compared to the single radial plasma observation. The technique also provides a better precision in the lower concentration range. The easy sample preparation and low detection limits combined with the high sample throughput of the method ensures low analysis costs.

References

[1] ASTM D4951:2014
[2] ASTM D5708:2015
[3] ASTM D5185:2018
[4] NF T60-106:2001-01-01
[5] DIN 51363:2008-08
[6] DIN 51390-4:2000-11
[7] DIN 51399-1:2017-02
[8] DIN 51400-10:2010-08
[9] DIN 51443-2:2012-01
[10] DIN EN 15944:2011-02
[11] P.W.J.M. Boumans, Spectrochim. Acta Part B: Atomic Spectroscopy 46, 431-445 (1991)

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