AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-165, Rev. 0

SPECTRO **ARCOS**

Analysis of Oils Using ICP-OES With Dual Side-On Plasma Observation

Introduction

A fast and simultaneous determination of trace elements, wear metals, additives and chlorine in oil can be performed using the SPECTRO ARCOS MultiView with dual side-on plasma observation. High precision, stability and low detection limits are achieved. A simple dilution of the sample provides an easy and reliable sample preparation step. The capability of the spectrometer to detect lines in the vacuum ultraviolet (VUV) enables the determination of halogens and the use of prominent lines for other elements in this region. In this report, sample preparation, line selection and detection limits of several elements in oils by ICP-OES are described.

The elemental analysis of oils is an important task for many petroleum laboratories and plays a key role in controlling refining processes. This test method covers the determination of additive elements, wear metals, additive packages and contaminants in used and unused lubricating oils and base oils according to ASTM 5185, ASTM 4951, ASTM 5708 and DIN 51577-5 [1-4].

Elements to be analyzed vary with the product. In crude oils, sulfur, alkali elements, vanadium, copper, nickel, iron and phosphorus are of importance to characterize the oil and to avoid deactivation of catalysts in the refining process. In lubricating oils, wear metals, such as aluminum, copper, nickel or iron, can indicate wear of any oil-wetted components and it can be determined 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 and the precision of the analytical results is critical in many cases. In waste oils, the determination of heavy metals, halogens and sulphur is of major importance.

Inductively coupled plasma optical emission spectrometry (ICP-OES) due to its multi element capability, high dynamic linear range, stability and low detection limits is accepted and/or suggested in several standard procedures for oil and fuel analysis [1-4].

Instrumentation

All measurements were performed with the SPECTRO ARCOS MultiView optical emission spectrometer with dual side-on plasma observation mode. It enables an average factor 2 enhanced sensitivity compared to single radial plasma observation and a comparable sensitivity to vertical torch dual-view systems, while eliminating typical axial-view interferences. The SPECTRO ARCOS features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique.

The SPECTRO ARCOS MultiView is equipped with CMOS detectors, avoiding blooming effects, allowing accurate measurement of trace concentrations even near intense matrix lines. 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 date.

The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the VUV/UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference-free lines in this region.

An air-cooled, 27.12 MHz free running type generator 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 with a cyclonic spray chamber was used. The operating conditions are given in Table 1.

Table 1 : ICP Operating Conditions

Power	1350 W
Plasma observation mode	DSOI
Coolant Flow	12 L/min
Auxiliary Flow	1.5 L/min
Nebulizer Flow	0.75 L/min
Plasma Torch	Quartz, fixed 1.8 mm Injector tube
Nebulizer	Noordermeer
Spray Chamber	Cyclonic
Sample aspiration rate	2ml/min
Replicate read time	20 sec per replicate

Calibration Standards

Calibration standards were prepared using a multi-element working standard with a concentration of 50 mg/kg by dilution with kerosene. The working standard was prepared from a 1,000 mg/kg Conostan oil standard (SCP Science, Baie D'Urfé QC, Canada). 0.04, 0.2, 0.4 and 1.2 g of the working standard were weighed and filled up to 20 g with kerosene and mixed well.

Cl and S standard solutions were prepared in the same way, weighing in single element standards of 10,000 mg/kg. For Cl, 0.01, 0.02 and 0.05 g and for S, 0.004, 0.01 and 0.02 g were weighed and filled up to 20 g with kerosene. The concentrations of the elements in the calibration standards are listed in Table 2.

Table 2: Calibration Standards

Element	Std.1 [mg/kg]	Std.2 [mg/kg]	Std.3 [mg/kg]	Std.4 [mg/kg]	Std.5 [mg/kg]	Std.6 [mg/kg]	Std.7 [mg/kg]	Std.8 [mg/kg]
Cl	0	2	10	20				
S	0	2	5	10				
Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn	0				0.1	0.5	1	3

For verification of the calibration, a control standard with a concentration of 0.26 mg/kg was prepared in the same way.

Results and Discussion

Table 3 shows the selected wavelengths and the limits of detections (LOD) achieved. The LODs were calculated according to the equation [4]:

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

Where:

RSD – relative standard deviation of 10 replicates of the blank [%]

c – concentration of the standard

SBR – signal to background ratio

The practical limits of detection depend on the dilution of the oil. The LODs were calculated considering a dilution factor of 10 and are expressed as µg/kg.

Table 3: Limits of detection (LOD) of the selected lines. The LODs were calculated considering a dilution factor of 10

Element	Line [nm]	LOD [µg/kg]
Ag	328.068	8
Al	167.078	5
B	249.773	10
Ba	455.404	3
Ca	393.366	0.5
Cd	214.438	3
Cl	134.724	2000
Co	228.616	10
Cr	205.618	7
Cu	324.754	20
Fe	259.941	7
K	766.491	200
Li	670.780	20

Element	Line [nm]	LOD [µg/kg]
Mg	279.553	0.2
Mn	257.611	1
Mo	202.095	10
Na	589.592	200
Ni	221.648	10
P	177.495	100
Pb	220.353	80
S	180.731	1000
Si	251.612	20
Sn	189.991	40
Ti	334.941	10
V	311.071	6
Zn	202.613	7

Accuracy

Table 4 shows excellent recoveries for the quality control standard.

Table 4: Recovery of the QC Standard

Element	QC Standard Concentration [mg/kg]	Measured Concentration [mg/kg]	Recovery [%]
Ag	0.261	0.258	99
Al	0.261	0.261	100
Ba	0.261	0.258	99
Ca	0.261	0.275	105
Cd	0.261	0.261	100
Co	0.261	0.262	100
Cr	0.261	0.263	101
Cu	0.261	0.267	102
Fe	0.261	0.264	101
K	0.261	0.251	96
Li	0.261	0.262	100
Mg	0.261	0.269	103
Mn	0.261	0.264	101
Mo	0.261	0.264	101
Na	0.261	0.249	96
Ni	0.261	0.260	100
P	0.261	0.275	105
Pb	0.261	0.260	100
Si	0.261	0.268	103
Sn	0.261	0.254	97
Ti	0.261	0.265	102
V	0.261	0.265	102
Zn	0.261	0.262	100

To confirm the accuracy of the calibration, a commercially available oil sample was spiked with 12 mg/kg Cl, 10 mg/kg S and 0.4 mg/kg of the other elements. Comparison of the results with the reference values shows good agreement for all the elements (Table 5).

Table 5: Spike Recovery analysis using commercial oil

Element	Measurement Sample Conc. [mg/kg]	Measured Sample + Spike Conc. [mg/kg]	Measured Spike Conc. [mg/kg]	Given Spike Conc. [mg/kg]	Spike Recovery [%]
Ag	0.001	0.35	0.35	0.38	92
Al	0.003	0.41	0.40	0.38	99
B	0.07	0.38	0.37	0,38	97
Ba	0.0004	0.33	0.35	0.38	92
Ca	0.003	0.376	0.37	0.38	97
Cd	0.0005	0.39	0.39	0.38	102
Cl	1.8	14.7	12.9	11.9	108
Co	< LOD	0.38	0.38	0.38	100
Cr	0.001	0.38	0.38	0.38	100
Cu	0.005	0.398	0.39	0.38	103
Fe	0.03	0.40	0.37	0.38	97
K	< LOD	0.38	0.38	0.38	100
Mg	0.002	0.376	0.37	0.38	97
Mn	0.0003	0.37	0.37	0.38	97
Mo	0.001	0.37	0.37	0.38	97
Na	0.03	0.35	0.35	0.38	92
Ni	< LOD	0.39	0.39	0.38	103
P	0.03	0.38	0.38	0.38	100
Pb	< LOD	0.38	0.38	0.38	100
S	7.6	17.7	10.1	9.7	104
Si	0.58	0.94	0.36	0.38	95
Sn	0.007	0.39	0.38	0.38	100
Ti	< LOD	0.36	0.36	0.38	95
V	< LOD	0.38	0.38	0.38	100
Zn	0.008	0.41	0.40	0.38	105

Conclusion

The SPECTRO ARCOS MultiView with dual side-on plasma observation offers a simple, fast, accurate and precise method for the simultaneous determination of trace elements, wear metals, additives as well as chlorine and sulfur in oil matrices. The easy sample preparation and low detection limits, combined with the high sample throughput of the method ensures low analysis costs and enables its use for various applications in petrochemistry.

References

[1] ASTM 5185: Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

[2] ASTM 4951: Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

[3] ASTM 5708: Standard Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry

[4] DIN 51577-5: Testing of lubricants – Determination of chlorine content – Part 5: Direct determination by optical emission spectral analysis with inductively coupled plasma (ICP OES)

[5] P. W. J. M. Boumans. Spectrochim. Acta 46B. 431 (1991)

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SPECTRO AMETEK

GERMANY
SPECTRO Analytical Instruments GmbH
Boschstrasse 10
D-47533 Kleve
Tel. +49.2821.892.0
spectro.sales@ametek.com

U.S.A.
SPECTRO Analytical Instruments Inc.
50 Fordham Rd
Wilmington 01887, MA
Tel. +1 800 548 5809
+1 201 642 3000
spectro-usa.sales@ametek.com

CHINA
AMETEK Commercial
Enterprise (Shanghai) CO., LTD.
Part A1, A4 2nd Floor Building No. 1 Plot Section
No. 526 Fute 3rd Road East; Pilot Free Trade Zone
200131 Shanghai
Tel. +86.400.022.7699
spectro-china.sales@ametek.com

Subsidiaries:
▸**FRANCE:** Tel. +33.1.3068.8970, spectro-france.sales@ametek.com ▸**GREAT BRITAIN:** Tel. +44.1162.462.950, spectro-uk.sales@ametek.com
▸**INDIA:** Tel. +91.22.6196.8200, sales.spectroindia@ametek.com ▸**ITALY:** Tel. +39.02.94693.1, spectro-italy.sales@ametek.com
▸**JAPAN:** Tel. +81.3.6809.2405, spectro-japan.info@ametek.co.jp ▸**SOUTH AFRICA:** Tel. +27.11.979.4241, spectro-za.sales@ametek.com