Improved productivity for the determination of metals in oil samples using the Agilent 5110 Radial View (RV) ICP-OES with Advanced Valve System

Application note

Petrochemical

Authors

Neli Drvodelic

Agilent Technologies
Melbourne, Australia

Introduction

The determination of metals in oils by ICP-OES using a radially-viewed plasma is a well established technique, especially for laboratories that implement ASTM Standard Test Method D5185-13. The method specifies ICP-OES for the rapid determination of 22 elements in used and unused lubricating oils and base oils, as well as rapid screening of used oils for wear-metals such as Fe, Cu and Al. Analysts use this test to monitor the condition of equipment for wear, to indicate the efficiency of the blending of additive packages, or for quality assurance of base oil for metal content [1].

The Agilent 5110 Radial View (RV) ICP-OES offers robustness, speed of analysis and reduced running costs. In this study, the 5110 RV was fitted with an Agilent SPS 4 Sample Preparation System and the fully integrated Agilent AVS 6 Advanced Valve System, which simplifies workflow and greatly improves productivity without compromising accuracy, precision, stability and repeatability. With the faster sample run times, the 5110 RV requires less argon gas per sample, which can lead to significant savings for labs involved in high throughput analysis.

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Experimental

Instrumentation

The Agilent 5110 RV ICP-OES was used for this analysis. The dedicated radial view (RV) configuration is ideal for the analysis of organic samples. The plug-and-play torch mechanism automatically aligns the vertical torch and connects all gases for fast start up while ensuring reproducible loading of the torch, independent of the operator. Mass flow controllers on the three gas lines into the torch as well as thermostatted optics facilitate long term stability of the emission signal as seen in the long term stability plot in Figure 2.

To run challenging samples, the RF system must be able to rapidly adjust to changes in the plasma conditions. The free running solid state radio frequency (SSRF) generator in the 5110 RV ICP-OES meets these challenges and can handle a wide range of organic samples, from volatile organics such as methanol or gasoline, to semi volatile organics such as kerosene. The benefit of this is that plasma conditions similar to those used for aqueous solutions can be used for organics without the need for high plasma gas flows. In addition, for the analysis of wear metals in kerosene based solvents, like A-Solv, there is no need for Ar/O_2 addition to the auxiliary gas flow or the use of a temperature controlled spray chamber.

An Agilent SPS 4 Sample Preparation System was used for automatic sample delivery in combination with a 6 port Advanced Valve System (AVS 6) [2]. The fully integrated AVS 6 utilizes a high speed pump to minimize uptake, and controlled bubble injection to aid with stabilization and washout, offering high throughput and excellent analytical performance for organic sample analysis.

The AVS 6 uses a positive displacement pump, requiring little maintenance in comparison to vacuum based pumps. Setup is easy, designed for simple assembly and disassembly, and is robust enough to handle tough samples, making it ideal for oil analysis.

The sample introduction system chosen for this analysis was the semi-volatile organics kit comprising of a glass concentric nebulizer, a 1.4 mm id RV torch, solvent resistant tubing, and a double-pass glass cyclonic spray chamber.

Instrument operating conditions are listed in Tables 1a and 1b.

Fitted background correction was used for all wavelengths, simplifying the method development by eliminating the need to determine off-peak background correction points for each element.

Table 1a. Agilent 5110 RV ICP-OES and 6 port Advanced Valve System (AVS 6) operating parameters

Parameter	Setting
Read time (s)	2
Replicates	2
Sample uptake delay (s)	4.5
Stabilization time (s)	6
Rinse time (s)	2 (fast pump: Off)
Pump speed (rpm)	12
RF power (kW)	1.30
Aux flow (L/min)	1.0
Plasma flow (L/min)	12.0
Nebulizer flow (L/min)	0.65
AVS 6 settings	
Loop volume (mL)	0.25
Pump rate: Valve uptake (mL/min)	36.0
Pump rate: Inject (mL/min)	10.0
Bubble injection time (s)	2.5
Pre-emptive rinse time (s)	1.5

Table 1b. Agilent 5110 RV ICP-OES method parameters

Parameters	Settings
Ar/O_2 addition	Not required
Nebulizer	Glass concentric
Spray chamber	Double Pass Cyclonic
Torch	Organic 1.4 mm id
Sample pump tubing	White-white SolvaFlex
Waste pump tubing	Grey-grey SolventFlex
SPS 4 rinse solution	Agilent A-Solv ICP solvent
Background correction	Fitted

The wavelengths selected for the analysis are given in Table 2. Wavelengths were selected according to the recommendations of ASTM D5185. Method Detection Limits (MDLs) are also given in Table 2. They are based on three sigma of ten replicate measurements of the blank solution during the analytical run and multiplied by ten (the sample dilution factor) to give the MDL in the original sample.

Table 2. Wavelengths used in the analysis. Method Detection Limits (MDLs) in the original sample are also shown.

Element and line	MDL (mg/kg)	Element and line	MDL (mg/kg)
Ag 328.068	0.020	Mn 257.610	0.0035
Al 396.152	0.13	Mo 202.032	0.089
B 249.772	0.032	Ni 231.604	0.269
Ba 233.527	0.029	Na 588.995	0.456
Ca 422.673	0.068	P 213.618	0.479
Cd 226.502	0.021	Pb 220.353	0.601
Cr 267.716	0.042	Si 288.158	0.115
Cu 324.754	0.032	Sn 189.925	1.40
Fe 259.940	0.049	Ti 334.188	0.023
K 766.491	0.83	V 311.837	0.022
Mg 285.213	0.049	Zn 213.857	0.028

Standard and sample preparation

Working standards of 0, 5, 10, 50 and 100 ppm were prepared from an Agilent A-21+K standard. This contains 22 elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn) at 500 ppm in oil. High concentration standards for Ba and Zn (200 ppm) and Ca, Cu, Fe and Mg (250 ppm) were prepared from 5000 ppm Single Element Standards in Hydrocarbon oil. These standards were matrix-matched for a constant viscosity using Base mineral oil (75 cSt) and diluted with Agilent A-Solv ICP solvent to give a total oil concentration of 10% (w/w) in each solution.

Used engine oil samples were diluted 1:10 (w/w) with A-Solv ICP solvent for the analysis. The samples were spiked with different concentrations of A-21+K to test the recoveries of wear metal elements and additive elements. Low concentration spikes were made at 25 ppm for all elements being determined. High concentration spikes, at 50 ppm for P and Zn, and 130 ppm for Ca were made. As with the standards, the samples were matrix-matched with the Base mineral oil to give a total oil concentration of 10% (w/w) in each solution.

Results and discussion

Linear calibrations were obtained with correlation coefficients greater than 0.999 for all wavelengths. This demonstrates the capability of the 5110 ICP-OES to detect low range (mg/kg) concentrations of elements in oil and at the same time monitor high concentrations of wear metals and additives with very high accuracy and precision. Figure 1 shows a calibration curve for Ca 422.673 up to 250 ppm with a correlation coefficient greater than 0.9999 and less than 3% calibration error on each calibration point. Because of the excellent linearity of the calibration curve, concentrations above the calibration range could be accurately measured, highlighting the achieved linear dynamic range (LDR) of the 5110 RV ICP-OES. The expansive LDR also allows the number of calibration standards to be reduced, which means more time can be spent running samples, and less time will be spent on calibration.

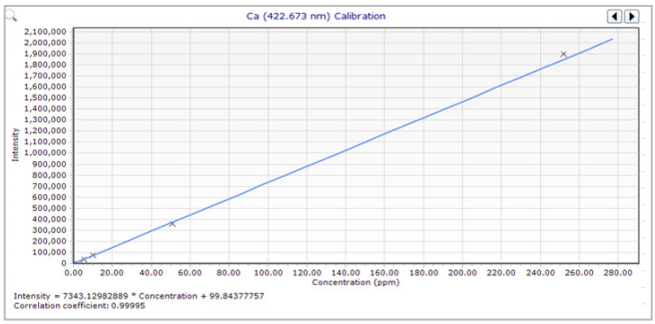

Figure 1. The calibration curve for Ca 422.673 nm up to 250 ppm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.0.99995.

All elements were determined in the oil samples in a single run. The spike recoveries obtained with the 5110 RV ICP-OES fitted with the AVS 6 are shown in Table 3. All values are within 10% of the expected values. Analysis time per sample was 22 seconds which includes a 2 second rinse between samples and a two replicate reading per sample. Total Ar consumption was only 7 L per sample.

Spike recoveries were also measured using the 5110 RV ICP-OES without the AVS 6 and similar recoveries were obtained. However, the analysis time was found to be 52 seconds, compared to just 22 seconds using the AVS 6. With the time saved using the AVS 6 you can more than double sample throughput and halve the argon consumption.

Table 3. Agilent 5110 ICP-OES spike recoveries for all elements in used engine oil. The 5110 was equipped with an SPS 4 autosampler and the integrated AVS 6.

Element and Line	Measured Engine Oil (mg/L)	Spike Amount (mg/L)	Measured Spike (mg/L)	Spike Recovery (%)	Element and Line	Measured Engine Oil (mg/L)	Spike Amount mg/L	Measured Spike (mg/L)	Spike Recovery (%)
Ag 328.068	0.004	24.95	24.23	97%	Mn 257.610	0.023	24.95	24.40	98%
Al 396.152	0.279	24.95	24.48	97%	Mo 202.032	4.977	24.95	30.91	104%
B 249.772	3.65	24.95	28.94	101%	Ni 231.604	<MDL	24.95	26.48	106%
Ba 233.527	0.041	24.95	24.73	99%	Na 588.995	0.874	24.95	24.71	96%
Ca 422.673	78.67	133.06	215.84	103%	P 213.618	36.21	49.23	86.96	103%
Cd 226.502	0.032	24.95	24.71	99%	Pb 220.353	0.019	24.95	26.65	107%
Cr 267.716	0.026	24.95	24.72	99%	Si 288.158	0.235	24.95	25.77	102%
Cu 324.754	0.147	24.95	24.20	96%	Sn 189.925	0.126	24.95	26.16	104%
Fe 259.940	0.413	24.95	26.02	103%	Ti 334.188	0.006	24.95	26.16	105%
K 766.491	0.054	24.95	23.97	96%	V 311.837	0.001	24.95	24.47	98%
Mg 285.213	0.364	24.95	24.96	99%	Zn 213.857	41.22	49.23	88.41	96%

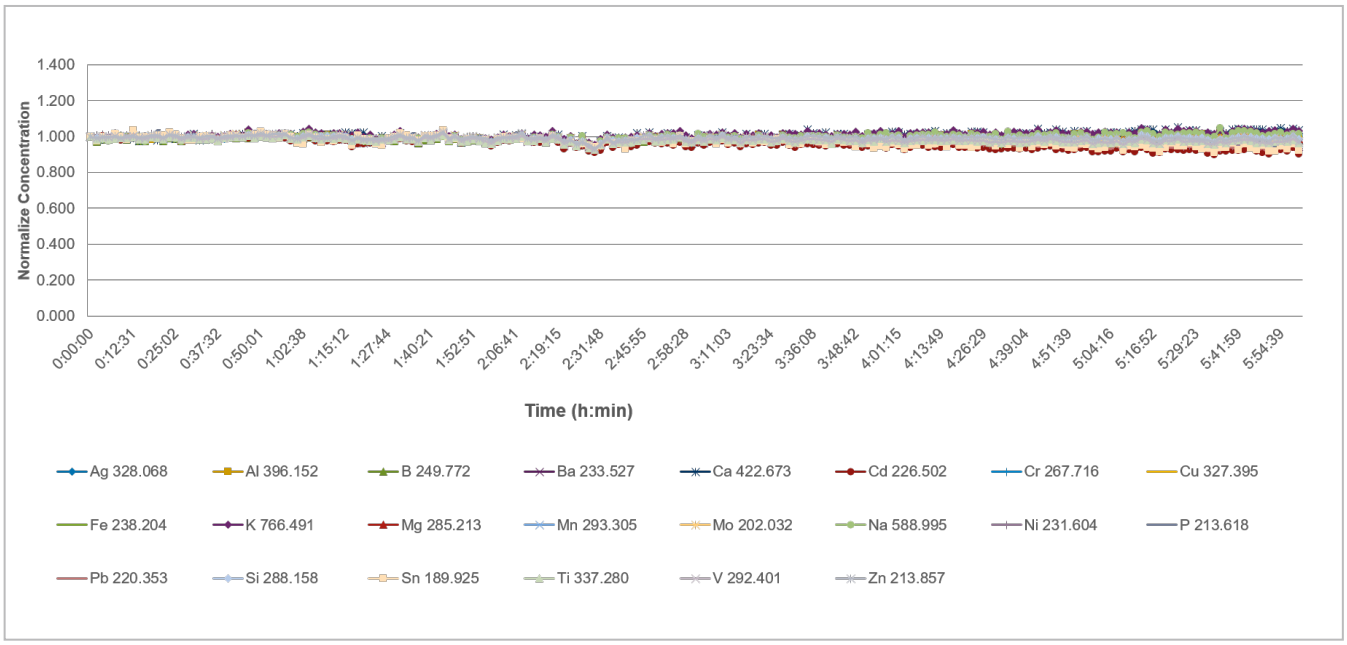

Figure 2. Stability plot over 6 hours for all elements in a used oil sample using the 5110 RV ICP-OES with an AVS 6.

Long term stability of the 5110 RV ICP-OES was evaluated by setting up a complete analytical sequence with 2 seconds rinse time between each sample and measuring a used engine oil sample every 5 samples over a 6 hour period. Over the entire run 1000 samples were analyzed without recalibration. The stability plot for all elements is displayed in Figure 2.

Precision ranged between 1.1 and 2.7 %RSD, with less than 10% deviation in concentration from the initial reading which demonstrates the robust sample handling capability of the vertically-oriented plasma in the 5110 RV ICP-OES, and the excellent precision of the instrument when using the Advanced Valve System (AVS 6).

Conclusions

The Agilent 5110 RV ICP-OES is the ideal instrument for determining metals in oil samples as per the ASTM D5185 method that is widely used by laboratories involved in the direct analysis of lubricating oils for wear metals and additives. The 5110 RV offers a number of advantages compared to other radial view ICP-OES:

- Sample analysis cycle time of 22 seconds per sample and total gas consumption of 7 L Ar per sample, when fitted with the Advanced Valve System (AVS 6), without compromising accuracy, precision or stability
- Sample analysis cycle time of 52 seconds per sample using the 5110 RV ICP-OES without the AVS 6
- Excellent long term stability with <3% RSD over 6 hours using the AVS 6
- A vertical plasma and robust 27 MHz SSRF system delivers matrix handling capability and robustness
- Simplified day-to-day operation and method development due to an intuitive software interface and fully integrated valving system
- Hardware features such as the plug-and-play torch lead to excellent method repeatability between operators and from instrument to instrument
- Improved productivity by reducing sample uptake, stabilization and washout time with the AVS 6 without compromising on performance.

Reference

1. ASTM D5185-13, Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

2. Reduce costs and boost productivity with the AVS 6 or 7 port switching valve system. Agilent publication no. 5991-6863EN.

www.agilent.com/chem

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