# Improved Productivity for the Determination of Metals in Oil Samples using the Agilent 5110 Radial View (RV) ICP-OES with Advanced valve system

Neli Drvodelic, Elizabeth Kulikov
Agilent Technologies Australia Pty Ltd

Agilent Technologies

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## 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.

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 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.

## Experimental

### Instrumentation

The Agilent 5110 RV ICP-OES was used for this analysis. The dedicated radial view (RV) configuration is ideally suited to 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. An Agilent SPS 4 was used for automatic sample delivery with a 6 port Advanced Valve System (AVS 6). 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 sample introduction system consisted of 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 1 and 2 and the wavelengths selected for the analysis are given in Table 3. Wavelengths were selected according to the recommendations of ASTM D5185. Method Detection Limits (MDLs) are also given in Table 3. They are based on three sigma of ten replicate measurements of the blank solution during the analytical run.

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## Experimental

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.

### Standard and sample preparation

- Working standards: 0, 5, 10, 50 and 100 ppm prepared from Agilent A-21+K standard
- 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
- Used engine oil samples were spiked with different concentrations of A21+K to test the recoveries of wear metal elements and additive elements, low concentration at 25 ppm
- High concentration spikes, at 50 ppm for P and 100 ppm and 200 ppm for Zn and Ca were made
- All solutions were matrix-matched using Base Mineral Oil (75 cSt) and diluted with kerosene to give a total oil concentration of 10 % (w/w) in each solution

**Table 1**. Agilent 5110 RV ICP-OES 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 |

**Table 2**. Agilent 6 port Advanced Valve System (AVS 6) settings

| Parameter | Setting |
|---|---|
| Sample 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 |

## Results and Discussion

### Linear Dynamic Range

Linear calibrations were obtained with correlation coefficient greater than 0.999 for all wavelengths. 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 range could be accurately measured, highlighting the achieved linear dynamic range (LDR) of the 5110 RV ICP-OES.

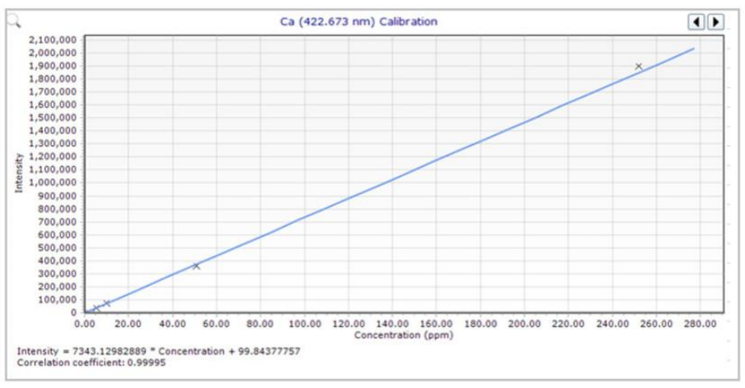


**Figure 1**. Calibration curve for Ca 422.673 nm up to 250 ppm shows excellent linearity

### Sample analysis and spike recoveries

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 the analysis time was found to be 52 seconds. With the time saved using the AVS 6 you can more than double sample throughput and halve the argon consumption.

## Results and Discussion

**Table3.** Used engine oil sample concentrations, spike recoveries, and method detection limits, acquired per ASTM method D5185-13. All results were determined in one analytical run. Note: measured spike recoveries for all elements listed in full application note.

| Element & line | MDL (mg/kg) | Unspiked Sample (ppm) | Spiked Level (ppm) | Recovery (%) |
|---|---|---|---|---|
| Ag 328.068 | 0.02 | 0.004 | 24.95 | 97 |
| Al 396.152 | 0.13 | 0.279 | 24.95 | 97 |
| B 249.772 | 0.032 | 3.65 | 24.95 | 101 |
| Ba 233.527 | 0.029 | 0.041 | 24.95 | 99 |
| Ca 422.673 | 0.068 | 78.67 | 133.06 | 103 |
| Cd 226.502 | 0.021 | 0.032 | 24.95 | 99 |
| Cr 267.716 | 0.042 | 0.026 | 24.95 | 99 |
| Cu 324.754 | 0.032 | 0.147 | 24.95 | 96 |
| Fe 259.940 | 0.049 | 0.413 | 24.95 | 103 |
| K 766.491 | 0.83 | 0.054 | 24.95 | 96 |
| Mg 285.213 | 0.049 | 0.364 | 24.95 | 99 |
| Mn 257.610 | 0.0035 | 0.023 | 24.95 | 98 |
| Mo 202.032 | 0.089 | 4.977 | 24.95 | 104 |
| Ni 231.604 | 0.269 | <MDL | 24.95 | 106 |
| Na 588.995 | 0.456 | 0.874 | 24.95 | 96 |
| P 213.618 | 0.479 | 36.21 | 49.23 | 103 |
| Pb 220.353 | 0.601 | 0.019 | 24.95 | 107 |
| Si 288.158 | 0.115 | 0.235 | 24.95 | 102 |
| Sn 189.925 | 1.40 | 0.126 | 24.95 | 104 |
| Ti 334.188 | 0.023 | 0.006 | 24.95 | 105 |
| V 311.837 | 0.022 | 0.001 | 24.95 | 98 |
| Zn 213.857 | 0.028 | 41.22 | 49.23 | 96 |

### Long Term Stability

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 samples 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 to 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 stability of the AVS 6.

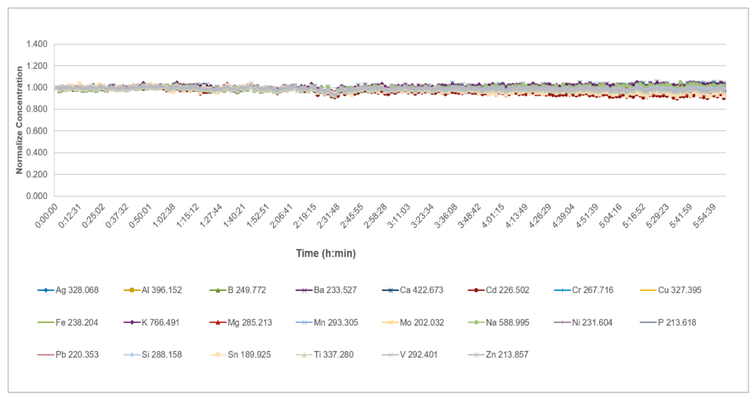


**Figure 2**. Stability plot over 6 hours for all elements in a used engine oil sample using the 5110 RV ICP-OES with the AVS 6

### Sample Measurement Time

A sample-to-sample analysis time of 22 seconds, with argon consumption of 7L per sample

22 elements were determined in all 1000 oil samples in a single run


## Conclusions

Oil samples were analyzed as per ASTM Method D5185-13, using the Agilent 5110 RV ICP-OES with sample introduction accessories.

The study found:

- A sample-to-sample analysis time of 22 seconds, with argon consumption of 7 L per sample when fitted with the Advanced Valve System (AVS 6)
- Excellent long term stability of <3 %RSD over 6 hours with the AVS 6
- A sample-to-sample analysis time of 52 seconds without the AVS 6
- All spike recoveries were within 10% of the expected values