Improved throughput for oils analysis by ICP-OES using next generation sample introduction technology

Application note

Energy and fuels

Author

B. Hahesy

Agilent Technologies
Melbourne, Australia

Introduction

The inductively coupled plasma optical emission spectroscopy (ICP-OES) technique for monitoring wear metal, additive and contaminant element levels in lubricating oils is the method of choice for predictive/preventive maintenance trend analysis across a range of industries. While long-term stability and repeatability/reproducibility are important, sample throughput is typically the most critical consideration.

This work outlines a method for the analysis of wear metals, additive and contaminant elements using a radial Agilent 725 Series ICP-OES. The Agilent SVS 2 Switching Valve System, a new and innovative sample introduction system, is used to improve sample throughput.

Agilent Technologies

A typical sample analysis cycle using ICP-OES involves sample uptake at high pump rates from the autosampler to the plasma, a stabilization delay to allow the plasma to come back into equilibrium, measurement of the sample and then a rinse of the sample from the system. A high-throughput contract lab measuring large numbers of samples on a daily basis using a conventional sample introduction system would typically measure a solution in about 1 to 2 minutes.

The SVS 2 improves the efficiency of sample introduction by greatly reducing sample uptake and washout times. This can result in more than a doubling of the sample throughput and significant reductions in operating costs. Since the flow of solution to the plasma is constantly maintained, there is an improvement in plasma stability and a reduction in stabilization times.

Experimental

Instrumentation
An Agilent 725 Series simultaneous ICP-OES with radially-viewed plasma, Agilent SPS 3 Sample Preparation System and SVS 2 Switching Valve System was used for this work.

The Agilent 725 features a custom-designed CCD detector, which provides true simultaneous measurement and full wavelength coverage from 167 to 785 nm. The patented CCD detector contains continuous angled arrays, which are matched exactly to the two-dimensional image from the echelle optics. The thermally-stabilized optical system contains no moving parts, ensuring excellent long-term stability.

The SVS 2 has two software-triggered valve positions. The first position allows the sample to be quickly loaded into a sample loop, ready to be aspirated into the plasma for measurement, using a positive displacement pump operating at up to 500 rpm. The controlling software then triggers the valves to switch and inject the sample into the ICP-OES utilizing the instrument peristaltic pump. In a typical analysis without the SVS 2, sample is fast-pumped into the plasma, producing an unstable signal for a short period, and requires a stabilization time of 10 to 15 seconds for the signal to settle prior to measurement. With the SVS 2, solution

is never directly injected into the plasma at high pump rates, ensuring much shorter stabilization delays can be used. In fact an uptake delay isn't required at all and a stabilization time of ~10 seconds can be sufficient to load the sample loop, inject the sample into the plasma and attain a stable signal. A system without the SVS 2 would typically require at least 25 seconds to perform the same function.

For a complete description of the SVS 2 throughput advantages, hardware and modes of operation see Reference 1.

Table 1 and Table 2 list the operating parameters used for the ICP-OES and SVS 2 during this analysis.

Table 1. ICP-OES instrument operating parameters.
Note: An all-glass sample introduction system (part number 9910117900) was used.

Condition	Setting
Power	1.35 kW
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	2.25 L/min
Spray chamber	Glass cyclonic double-pass (Twister)
Torch	One-piece quartz radial torch (1.5 mm id injector)
Transfer tube	Glass
Nebulizer	Glass concentric (SeaSpray)
Nebulizer flow rate	0.55 L/min
Viewing height	9 mm
Pump tubing	
Rinse/instrument pump	Gray/gray SolventFlex (1.30 mm id)
Waste	Purple/black SolventFlex (2.29 mm id)
Pump speed	12 rpm
Total sample usage	2 mL
Replicate read time	2 s
Number of replicates	3
Sample uptake delay	0 s
Stabilization time	12 s
Rinse time	0 s
Fast pump	Off
Background correction	Fitted

Table 2. SVS 2 operating parameters.
Note: The internal standard/diluent channel was not used.

Condition	Setting
Loop uptake delay	7 s
Uptake pump speed — refill	500 rpm
Uptake pump speed — inject	150 rpm
Sample loop size	0.5 mL
Time in sample	6 s
Bubble inject time	6.9 s

Standard and sample preparation

Calibration solutions of 0, 5, 10, 25 and 50 mg/L were prepared from Conostan S-21 + K certified standard, which 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 mg/kg in oil. These calibration solutions were viscosity-matched using Conostan Element Blank Oil (75 cSt) and diluted with kerosene to give a total oil concentration of 10% (w/v) in each solution.

Duplicate 0.5 g portions of NIST SRM 1084a (Wear-Metals in Lubricating Oil) and 2 g of Element Base Oil were accurately weighed into 25 mL volumetric flasks and made up to volume with kerosene. A third 0.5 g portion was similarly prepared, spiked with S-21 + K standard.

Duplicate 0.5 g portions of NIST SRM 1085b (Wear-Metals in Lubricating Oil) and 4.5 g of Element Base Oil were accurately weighed into 50 mL volumetric flasks and made up to volume with kerosene.

Results and discussion

Method detection limits (MDLs)

3σ method detection using the operating parameters defined in Table 1 and Table 2 are shown in Table 3.

All detection limits are well below 0.2 mg/L, allowing wear metals to be detected and a trend observed even at low levels.

Table 3. Detection limits

Element and wavelength	MDL (mg/L)
Ag 328.068	0.003
Al 308.215	0.018
B 249.678	0.011
Ba 493.408	0.002
Ca 422.673	0.008
Cd 228.802	0.005
Cr 205.560	0.010
Cu 327.395	0.007
Fe 259.940	0.004
K 766.491	0.081
Mg 285.213	0.006
Mn 260.568	0.004
Mo 204.598	0.015
Na 588.995	0.062
Ni 230.299	0.018
P 177.434	0.069
Pb 283.305	0.031
Si 251.611	0.101
Sn 283.998	0.128
Ti 334.941	0.002
V 292.401	0.003
Zn 213.857	0.015

Linearity

The correlation coefficients (r^2) for each calibration are shown in Table 4.

All r^2 values are >0.999 for each element, displaying excellent linearity across the range of 0–50 mg/L (equivalent to a maximum measurable sample concentration of ~500 mg/kg using a 10-fold w/v dilution). For additive elements (such as calcium, magnesium and phosphorus) where a higher maximum measurable concentration may be necessary, the linear range can be further extended by using higher concentration calibration standards and selecting less sensitive wavelengths (where necessary). The wavelengths selected for analysis may reflect a compromise between the required detection limits

and concentration ranges (where a single wavelength is chosen for each element), or alternatively multiple wavelengths may be selected for each element and MultiCal applied to provide low detection limits and high maximum measurable concentrations.

Table 4. Linearity

Element and wavelength	r^2
Ag 328.068	0.9998
Al 308.215	0.9998
B 249.678	0.9998
Ba 493.408	0.9996
Ca 422.673	0.9996
Cd 228.802	0.9999
Cr 205.560	0.9999
Cu 327.395	0.9997
Fe 259.940	0.9999
K 766.491	0.9996
Mg 285.213	0.9998
Mn 260.568	0.9998
Mo 204.598	0.9999
Na 588.995	0.9999
Ni 230.299	0.9999
P 177.434	0.9999
Pb 283.305	0.9997
Si 251.611	0.9999
Sn 283.998	0.9999
Ti 334.941	0.9997
V 292.401	0.9999
Zn 213.857	0.9999

Washout/carryover

The minimal swept volume of the SVS 2 sample path, and reduced sample contact time with the remainder of the introduction system minimizes the required rinse time. Since rinsing of the nebulizer and spray chamber is performed during the sample uptake time and rinsing of the sample uptake tubing is performed during the analysis time, rinse delays can be virtually eliminated. By adjusting the uptake delay and fast uptake pump speed during the refill and inject phases via the SVS 2 software, rinsing of the introduction system can be optimized for the required analysis.

Carryover was assessed by analyzing successive standard/blank pairs and calculating the measured blank concentrations as a percentage of the actual standard concentration. The carryover from a 500 mg/L iron standard and 200 mg/L barium, calcium, copper, magnesium and zinc standards was evaluated and the results are shown in Table 5. For each of the elements monitored there was no increasing trend, and carryover did not exceed 0.1%, demonstrating that a sample washout of greater than three orders of magnitude can be achieved with no additional rinse time added to the analysis sequence.

Analytical results

While the emphasis on accuracy for wear metals analysis is not as great as for many other types of analysis (results are used for trend analysis only), NIST Standard Reference Materials 1084a and 1085b were analyzed using the operating parameters as defined in Table 1 and Table 2 and their results reported in Table 6 and Table 7.

Table 5. Washout/carryover

Blank measurement	Carryover (% of standard concentration)					
	Ba 493.408	Ca 422.673	Fe 259.940	Cu 327.395	Mg 285.213	Zn 213.857
1	0.039	0.047	0.035	0.043	0.045	0.027
2	0.039	0.032	0.032	0.046	0.057	0.026
3	0.052	0.034	0.035	0.039	0.058	0.037
4	0.050	0.034	0.038	0.040	0.047	0.037

Table 6. NIST SRM 1084a, Wear-Metals in Lubricating Oil — sample source NIST US Department of Commerce.
Note: Values in parentheses '()' not certified (information only).

Element and wavelength	Certified (mg/kg)	Found (mg/kg)	Duplicate (mg/kg)	Recovery (%)	RPD dup. (%)	Spike level (mg/L)	Recovered (mg/L)	Recovery (%)
Ag 328.068	101.4	100.3	101.1	98.9	0.9	2.17	2.27	104.6
Al 308.215	(104)	99.7	100.4	95.9	0.7	2.17	2.27	104.3
Cr 205.560	98.3	104.3	105.5	106.1	1.2	2.17	2.27	104.3
Cu 327.395	100.0	102.7	103.6	102.7	0.8	2.17	2.27	104.5
Fe 259.940	98.9	105.2	105.4	106.4	0.2	2.17	2.25	103.5
Mg 285.213	99.5	102.5	102.9	103.0	0.4	2.17	2.28	104.9
Mo 204.598	100.3	106.2	106.3	105.9	0.1	2.17	2.28	104.9
Ni 230.299	99.7	106.2	107.0	106.5	0.7	2.17	2.28	104.9
Pb 283.305	101.1	103.1	105.7	102.0	2.5	2.17	2.30	105.9
Si 251.611	(103)	100.2	100.4	97.3	0.2	2.17	2.31	106.1
Sn 283.998	97.2	105.8	105.6	108.8	0.2	2.17	2.31	106.3
Ti 334.941	100.4	105.2	105.2	104.8	0.0	2.17	2.27	104.5
V 292.401	95.9	105.4	105.9	109.9	0.4	2.17	2.30	106.0

NIST SRM 1084a

Even with the high dilution factor used in the preparation of the analyzed solutions, the recovery data shows very good agreement with the specified values, all results being within ±10% of the stated values and the relative percent difference (RPD) of the duplicate analysis within 2.5% for each element. The sample spike results are also very good with recoveries for all elements well within ±10% of the spiked concentration.

NIST SRM 1085b

Once again the recovery data shows very good agreement with the specified values, all results being well within ±10% of the stated values and the relative percent difference (RPD) of the duplicate analysis within 5% for each element.

System stability

A 5 mg/L solution was analyzed every 10 samples over a period of six hours (without internal standardisation or recalibration) and the recoveries calculated. The trend of results for each element/wavelength is a measure of the stability of the system. Figure 1 illustrates that conditions remain stable for the duration of the six hour period with all results well within ±10% and precision less than 2% RSD.

Speed of analysis

Use of the SVS 2 sample introduction system dramatically reduced analysis time when compared to traditional introduction systems. Using the operating parameters defined in Table 1 and Table 2 the tube to tube analysis time for this study averaged 33 seconds during a one hour sequence, equating to >100 samples/ hour.

Table 7. NIST SRM 1084a, Wear-Metals in Lubricating Oil — sample source NIST US Department of Commerce.
Note: Values in parentheses '()' not certified (information only), values in brackets '{}' not certified (reference only).

| Element and wavelength	Certified (mg/kg)	Found (mg/kg)	Duplicate (mg/kg)	Recovery (%)	RPD dup. (%)
Ag 328.068	304.6	307.0	315.9	100.8	2.9
Al 308.215	{300.4}	300.8	306.6	100.1	1.9
B 249.678	(300)	312.4	327.8	104.1	4.9
Ba 493.408	(314)	331.3	339.1	105.5	2.4
Ca 422.673	(298)	292.7	300.6	98.2	2.7
Cd 228.802	302.9	305.1	310.8	100.7	1.8
Cr 205.560	302.9	324.1	329.7	107.0	1.7
Cu 327.395	295.6	303.0	311.1	102.5	2.7
Fe 259.940	{301.2}	310.7	316.9	103.1	2.0
Mg 285.213	297.3	303.6	309.8	102.1	2.1
Mn 260.568	(289)	291.3	296.8	100.8	1.9
Mo 204.598	(296)	312.7	317.8	105.6	1.6
Na 588.995	305.2	299.4	309.7	98.1	3.5
Ni 230.299	295.9	315.5	319.7	106.6	1.3
P 177.434	{299.9}	317.0	317.4	105.7	0.1
Pb 283.305	297.7	308.7	313.2	103.7	1.5
Si 251.611	{300.2}	315.1	314.8	105.0	0.1
Sn 283.998	(294)	317.2	322.7	107.9	1.7
Ti 334.941	{301.1}	311.5	317.2	103.5	1.8
V 292.401	297.8	309.1	314.5	103.8	1.8
Zn 213.857	296.8	308.8	314.9	104.1	2.0
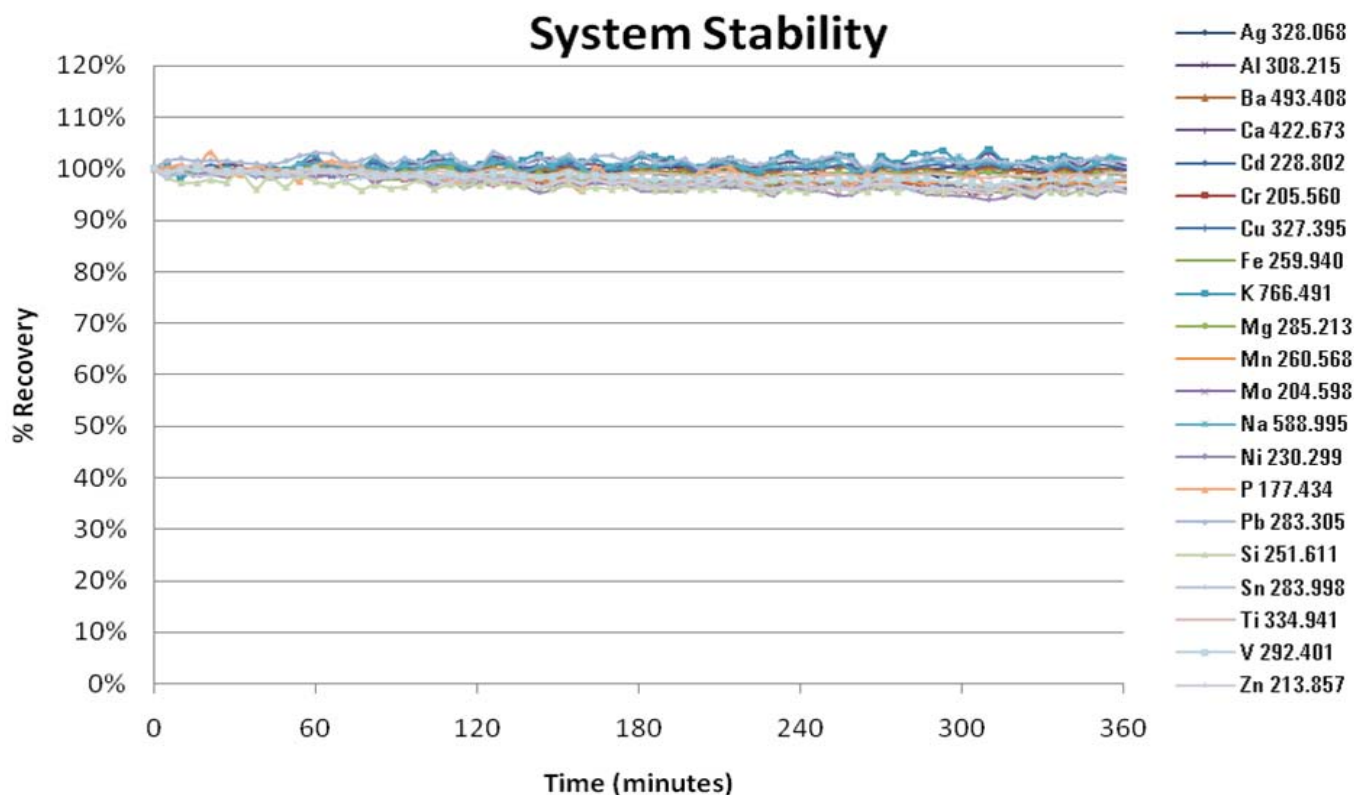
Figure 1. System stability

Conclusion

Using the SVS 2 with an Agilent 725 Series radially-viewed ICP-OES and SPS 3 sample preparation system more than halved the average sample analysis cycle time of 90 seconds without the SVS 2 to 33 seconds per sample using the SVS 2 (equating to >100 samples/hour), without compromising accuracy, precision or stability.

Since the sample does not make contact with peristaltic pump tubing prior to being aspirated into the plasma, the inert sample path and minimal swept volume results in greatly reduced sample carryover.

References

1. Hoobin, D. & Vanclay, E. (2010). Ultra-fast ICP-OES determinations of soil and plant material using next generation sample introduction technology. Agilent application note, publication number SI-02448.

2. ASTM Designation D 5185-09 (2009). 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).

3. National Institute for Standards and Technology certificates of analysis. Gaithersburg, Maryland, USA.

www.agilent.com/chem

Agilent Technologies