Application for Energy and Fuels

Improved Throughput for Wear Metals Analysis by ICP-OES Using Next Generation Sample Introduction Technology

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Typical Aqueous Application Conditions

Ultra-fast ICP-OES determinations of base metals in geochemical samples using next generation sample introduction technology

Application note

Geochemistry, mining and metals

Details:

- Four-acid digest: HCl, HNO3, HClO4 and HF
- Calibration: stabilized with 30% v/v HCl
- Typical low flow plasma conditions
- High throughput with SVS-2

Condition	Setting
Power	1.2 kW
Plasma gas flow rate	10.5 L/min
Auxiliary gas flow rate	1.5 L/min
Spray chamber type	Glass cyclonic (double-pass)
Torch	Standard one piece quartz radial
Viewing height	10 mm
Nebulizer type	OneNeb
Nebulizer flow rate	0.8 L/min
Pump tubing	Rinse/instrument pump: Black-black tabs (0.76 mm ID)
	Waste: blue-blue tabs (1.65 mm ID)
Pump speed	20 rpm
Replicate read time	3 s
Number of replicates	3
Sample uptake delay time	0 s
Stabilization time	20 s
Rinse time	0 s
Fast pump	Off

Organic Application Considerations

The challenge:

- High vapour pressure from solvents
  - Plasma instability
  - Extinguished plasma
- Carbon build up on injector
  - Poor precision and drift
  - Down time - injector requires regular cleaning
- Nebulizer blockage
  - Poor precision
  - Down time - nebulizer needs cleaning

Organic Application Considerations

The solution:

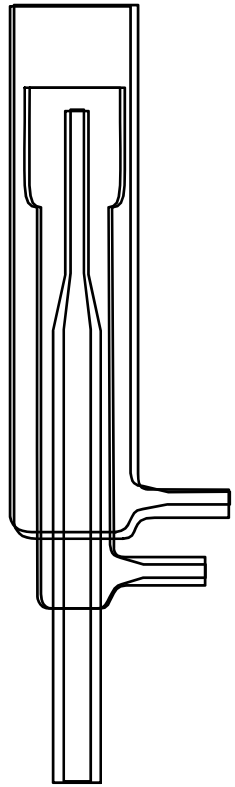
- Carbon build up
  - Use radially viewed vertically oriented plasma
    - Minimizes carbon build-up
    - Exhaust positioned directly above plasma, efficiently extracts carbon by-products
  - Use oxygen addition into auxiliary gas flow to facilitate removal of carbon and reduce background
    - Mandatory with axial ICP

- Nebulizer blockage
  - Use nebulizer with large ID to reduce blockage from particulates
    - e.g. SeaSpray, Slurry or V-groove nebulizer
  - Use new OneNeb nebulizer
  - Filter samples or allow to settle and sample from the top
    - Conikal nebulizer produces finer aerosol

One Piece Torches

Radial ICP Torches

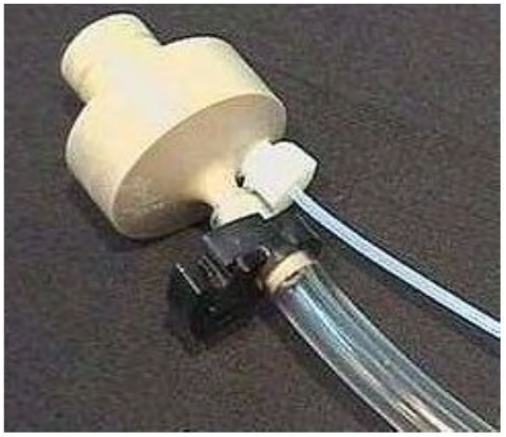
- Designed specially for organic solvents
- Annealed for greater durability
- Choice of 0.8 and 1.4mm ID. injector
  - 1.4 mm ID suitable for organic solvents of low to moderate volatility
  - 0.8 mm ID suitable for highly volatile organic solvents



Nebulizers

- Sample particulates may block standard concentric nebulizers
  - Dependent on sample composition e.g. wear metal particulates
  - Poor precision
  - Down time - nebulizer needs cleaning
- Quartz nebulizer
  - Conikal, Seaspray and Slurry
  - Faster washout
- V-groove nebulizer
  - Made of PEEK polymer
  - Minimizes particulate blockage

Quartz nebulizer

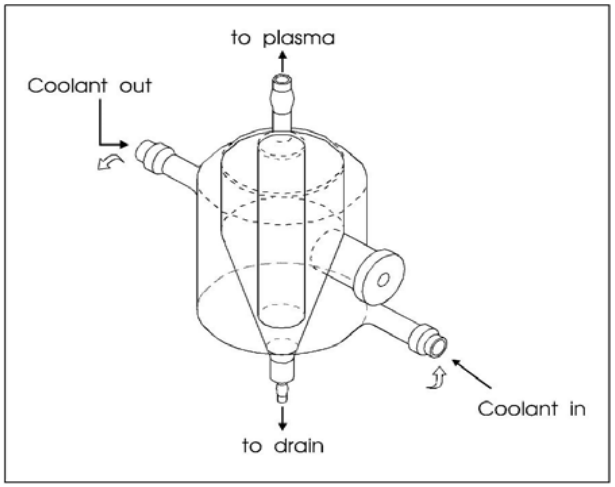


V-groove nebulizer

Spray Chambers

- **Double-pass glass cyclonic spray chamber**
  - Double pass design
  - Reduces solvent load
  - Increased sensitivity
  - Fast washout
  - Suitable for low vapour organic solvents

- **Cooled spray chamber**
  - Externally jacketed or Peltier cooled designs
  - Can cool sample to -10 ^{o}C or lower
  - Reduces solvent load
  - Made of quartz
  - Excellent for highly volatile organic solvents e.g. naphtha



Compatibility of Pump Tubing

Pump Tubing

Solvent	PVC	Viton	PVC Solva
Kerosene	✗	✓	✓
Gasoline	✗	✓	✗
Fuel	✗	✓	✗
Coolant	✓	✓	N/A

✗ = unsatisfactory, ✓ = satisfactory, N/A = no data available

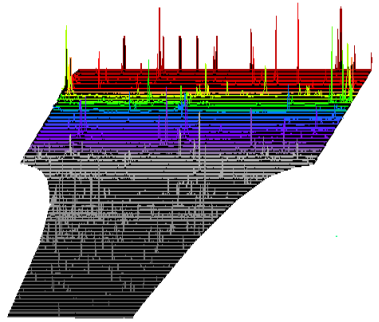
Organic Application Considerations

The challenge:

- Various elements of interest
  - May need to calibrate for 30 to 60 different elements
- Unknown concentration of analytes in samples
  - Down time – to perform multiple dilutions for the same sample
- Difficult interferences to overcome
  - Poor accuracy

700 Series Optical Design

Echelle Optical Design



Full wavelength coverage

- Maximum flexibility for extended linear working range
- Elimination of spectral interferences

All wavelengths captured in one reading

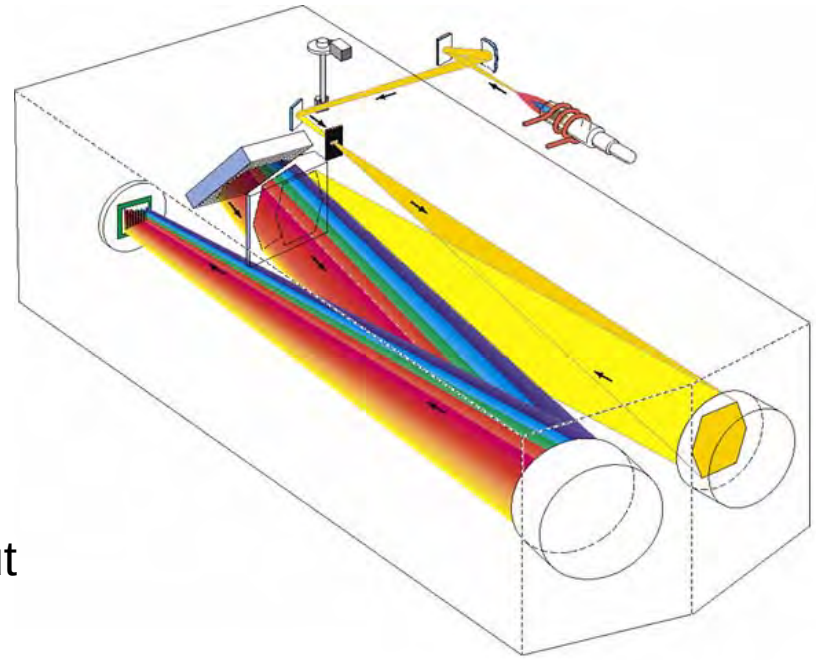
- Maximum speed and productivity

Fewer optical components

- Excellent signal-to-noise
- Lowest detection limits

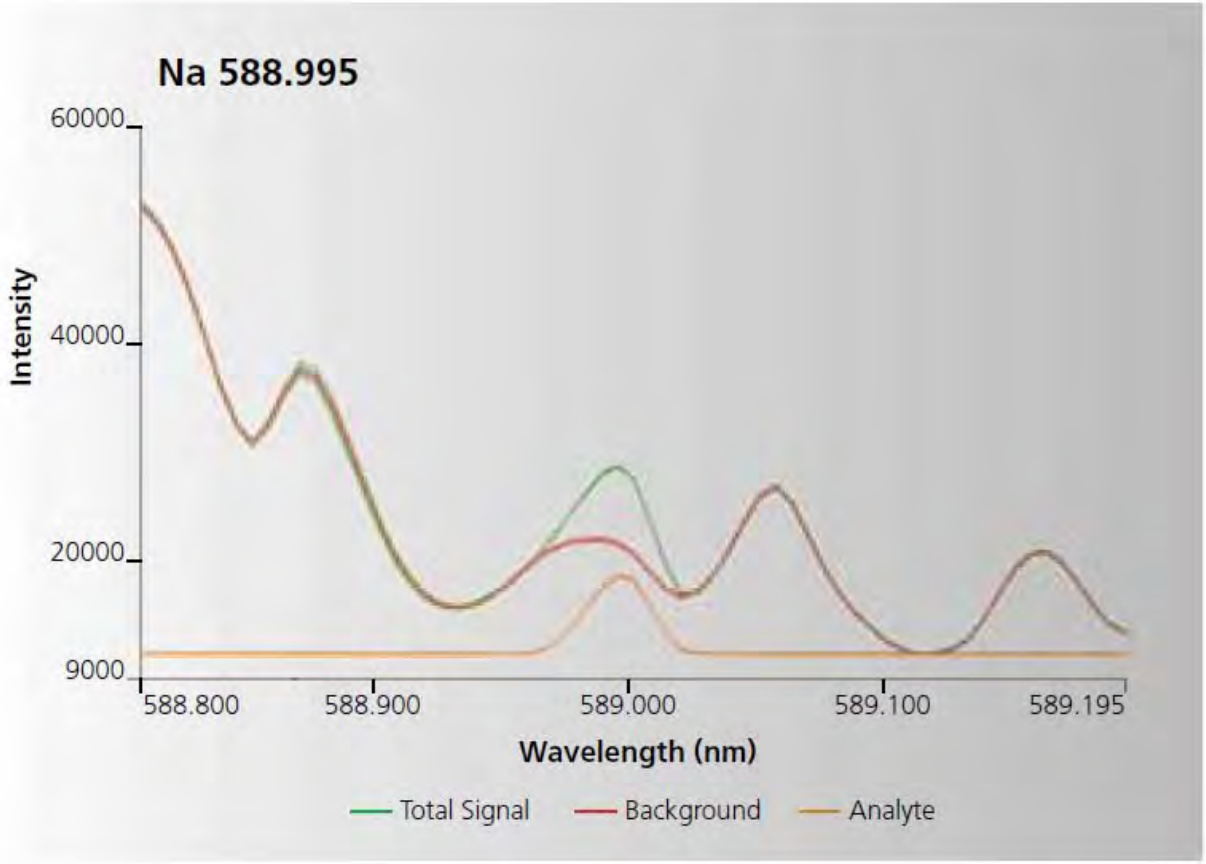
Thermostatted to 35°C

- Excellent long term stability
- Fast start-up, increasing sample throughput



Structured Background from Na 589nm in Oil

- Diluted in white spirit FACT Corrected



FACT removes complex organic background structures providing accurate determination of low level sodium in used oils.

Measuring Petroleum Products Successfully

The solution:

- Linear dynamic range
  - Use wavelength flexibility to extend the upper limit
  - Still achieve best detection limits
- Structured backgrounds
  - Radial ICP-OES
  - Use patented Fast Automated Curve-fitting Technique (FACT)
- Speed of analysis
  - 725 simultaneous CCD system
  - Fastest possible read out speed

Sample and Standard Preparation

Sample Preparation

- Up to 1 in 10 dilution on a weight per volume basis
- Use suitable organic solvent e.g. xylene, kerosene, Shellsol

Standard Preparation

- Multi-element organometallic standard (e.g. Conostan S-21)
- Select dilution ratio to achieve required concentration
- Add extra neutral base oil (No. 75) to ensure consistent viscosity

Typical Organic Instrument Conditions

Plasma power	1.3 - 1.5kW
Plasma gas flow	15 – 18 L/min
Auxiliary gas flow	0.75 – 2.25 L/min
	(axial – radial)
Nebulizer gas flow (axial)	Optimize
	(0.5 – 0.8 L/min)
Nebulizer gas flow (radial)	Set bullet to top of torch
	(0.5 – 0.8 L/min)
AGM-1 setting	2 - 6
Stabilization delay	Optimize via time scan
Pump speed	5 - 10 rpm
Uptake Rate	< 1 mL/min
Fast Pump	Yes or No?

Wear Metals Analysis

A High Throughput Application

Accuracy

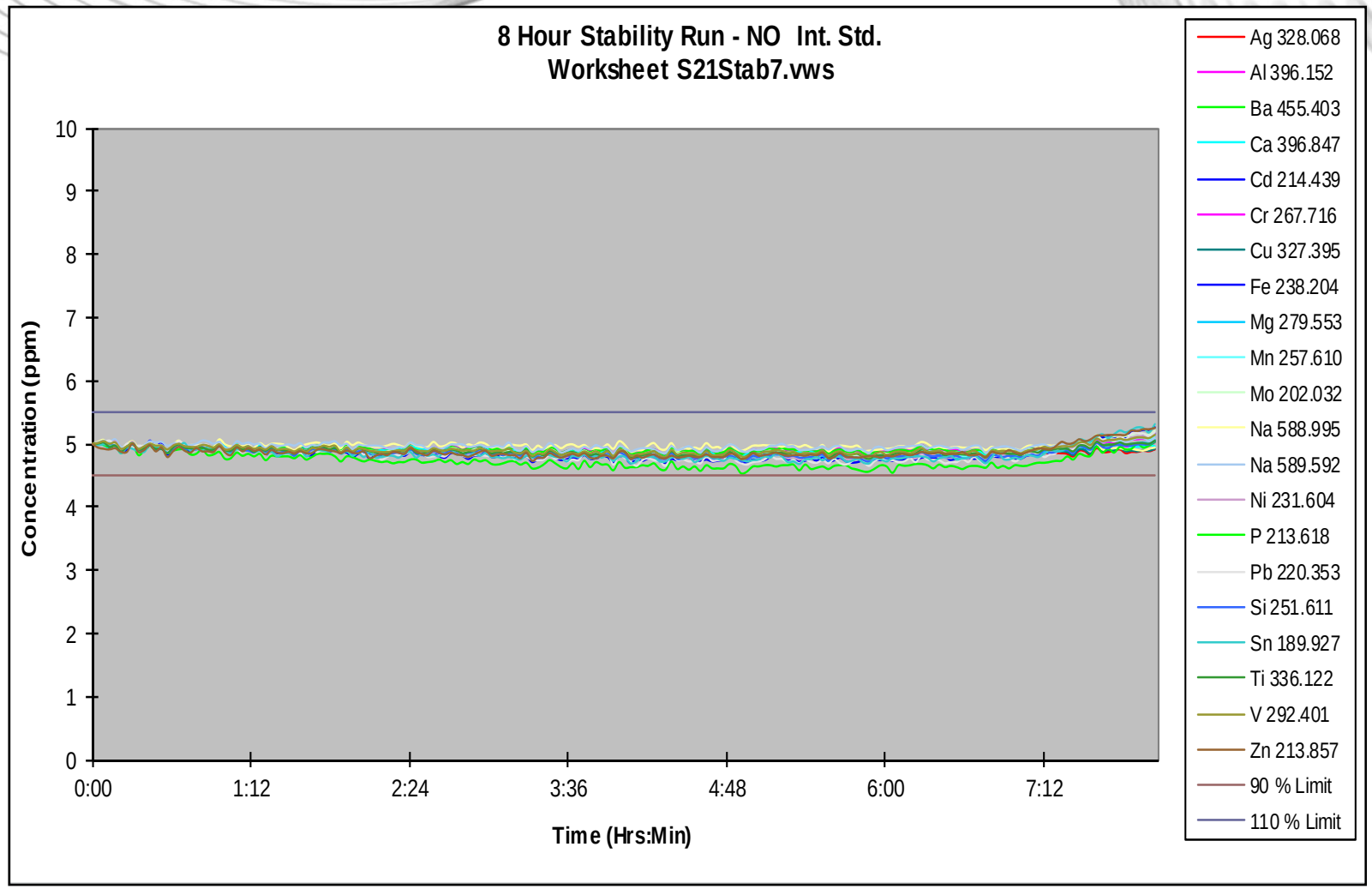
CRM Analysis 1084a Wear metals in lubricating oil

Elements & Wavelength (nm)	Results (ppm)	CRM 1084a (ppm)	% Recovery
Ag 328.068	96.3	101.4	95
Al 167.019	105.6	104	102*
Cr 267.716	96.9	98.3	99
Cu 327.395	99.1	100	99
Fe 238.204	100.6	98.9	102
Mg 279.553	100.6	99.5	101
Mo 202.032	96.6	100.3	96
Ni 231.604	99.5	99.7	100
Pb 220.353	107.7	101.1	107
S 181.972	2022	1700	119**
Si 251.611	100.7	103	98*
Sn 189.927	91.5	97.2	94
Ti 336.122	101.3	100.4	101
V 292.401	101.3	100.4	101

*** Uncertified results**

**** Uncertified results, result was high because of kerosene contamination**

Plasma Stability



Eight hour stability run for elements in oil/kerosene - Conostan S21

Introduction

In order to predict when equipment maintenance may be required or to prevent having to perform maintenance, lubricating oils in equipment are regularly analyzed to monitor changes in levels of wear-metals, and additive and contaminant elements. The analyst is mainly interested in trending changes over time, not exact values. So high sample throughput could be considered more important than accuracy, precision, long-term stability and repeatability/reproducibility.

In this work, an **Agilent 725 Series ICP-OES** inductively coupled plasma optical emission spectrometer with **Agilent SPS 3 Sample Preparation System** and **Agilent SVS 2 Switching Valve System** was used. The SVS 2 improves efficiency by greatly reducing sample uptake and washout times. The typical ICP-OES sample analysis cycle time was halved (to 33 seconds per sample), significantly reducing operating costs, without compromising accuracy, precision, long-term stability and repeatability/reproducibility.

Measurement challenge

Challenge

While long-term stability and repeatability/reproducibility are important in wear-metal analysis, since analytical results are used only for trend analysis, accuracy becomes a less important factor and sample throughput is often the most critical consideration.

Solution

Using the Agilent SVS 2 Switching Valve System with an Agilent 725 Series radially-viewed ICP-OES and Agilent SPS 3 Sample Preparation System more than halves the sample analysis cycle time of about 90 seconds without the SVS 2, to about 33 seconds per sample using the SVS 2, without compromising accuracy, precision or stability.

Experimental
Instrumentation

- Instrument: Agilent 725 Series simultaneous ICP-OES with radially-viewed plasma.
- Accessories: Agilent SPS 3 Sample Preparation System; Agilent SVS 2 Switching Valve System.

725 ICP-OES

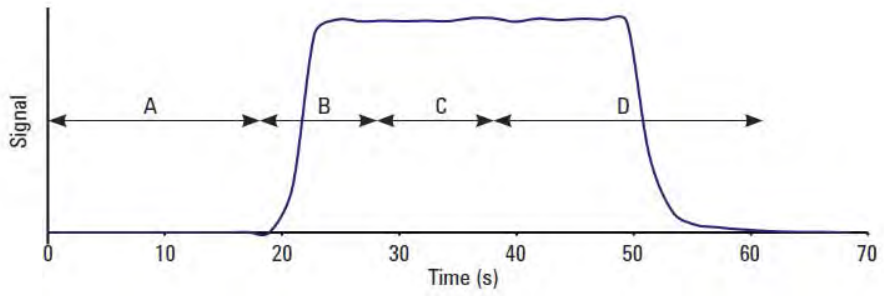
Switching Valve System 2
Increase Productivity

- Higher sample throughput
- Decreased wear and tear on nebulizer/spraychamber/torch
- Lower operating cost through reduced argon use

SVS Productivity Packages

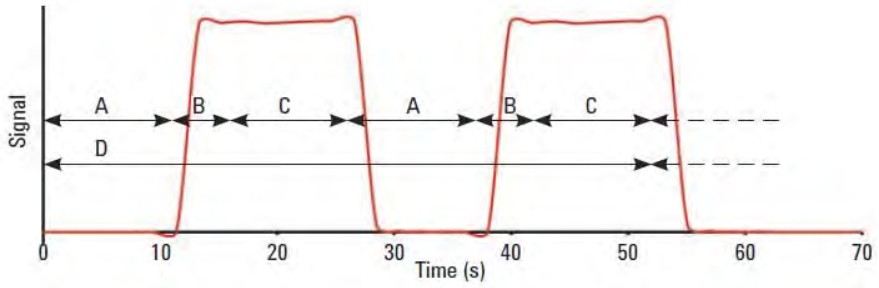
How does it work?

Without SVS



With SVS 2

- More than double your throughput
- Continuous rinsing
- Faster sample uptake
- Shorter stabilization delays

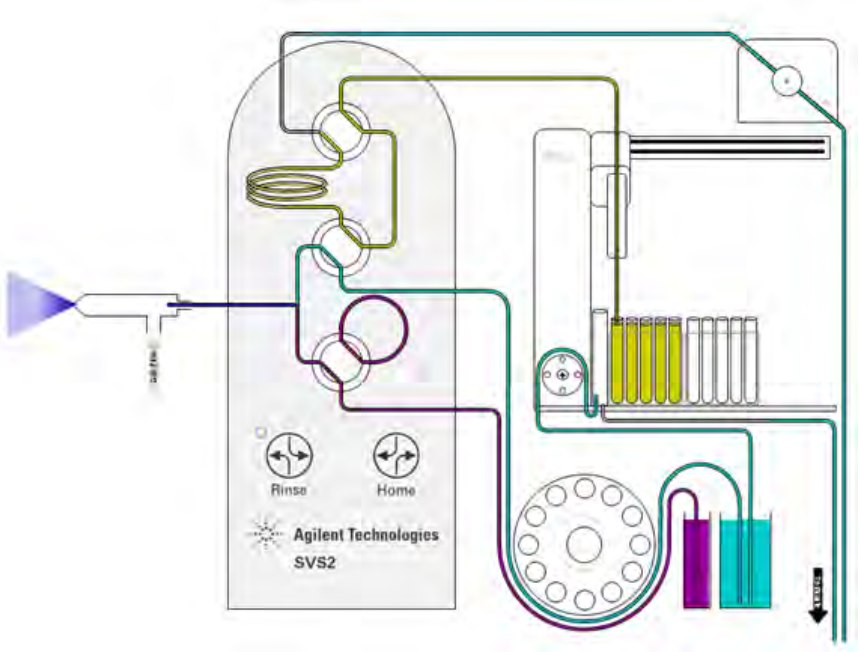


Comparison of the sample uptake, measurement and rinse profiles of 100 mg/L manganese without a SVS and the SVS 2. The data shows a dramatic increase in productivity while maintaining consistent data quality.

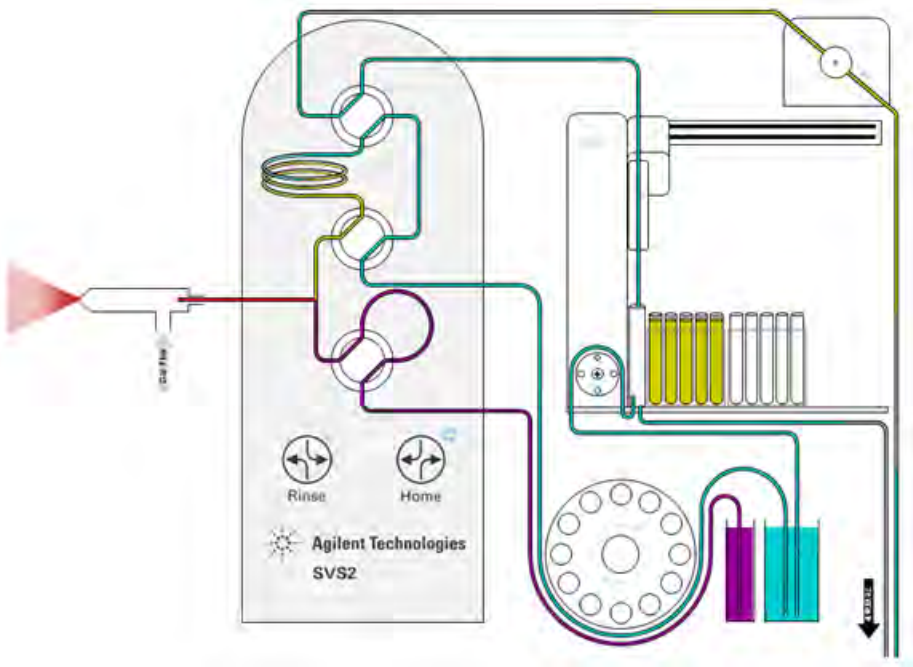
SVS 2 Switching Valve System

Second Generation Switching Valve

SVS 2 in Sample Load Position



SVS 2 in Sample Inject Position



Load ⟷ Analyze

Experimental
Instrumentation

Agilent 725 Series ICP-OES instrument operating parameters

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 (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: 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

Note: An all-glass sample introduction system (part number 9910117900) was used.

Experimental
Instrumentation

Agilent SVS 2 Switching Valve System operating parameters

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

Note: The internal standard/diluent channel was not used.

Experimental

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.

Experimental

3σ method detection limits (MDLs) & linearity correlation coefficients

Element &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

Element &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

Results
NIST SRM 1084a

Wear-metals in lubricating oil – sample source NIST US Department of Commerce.
Note: Values in parentheses "()" not certified (information only).

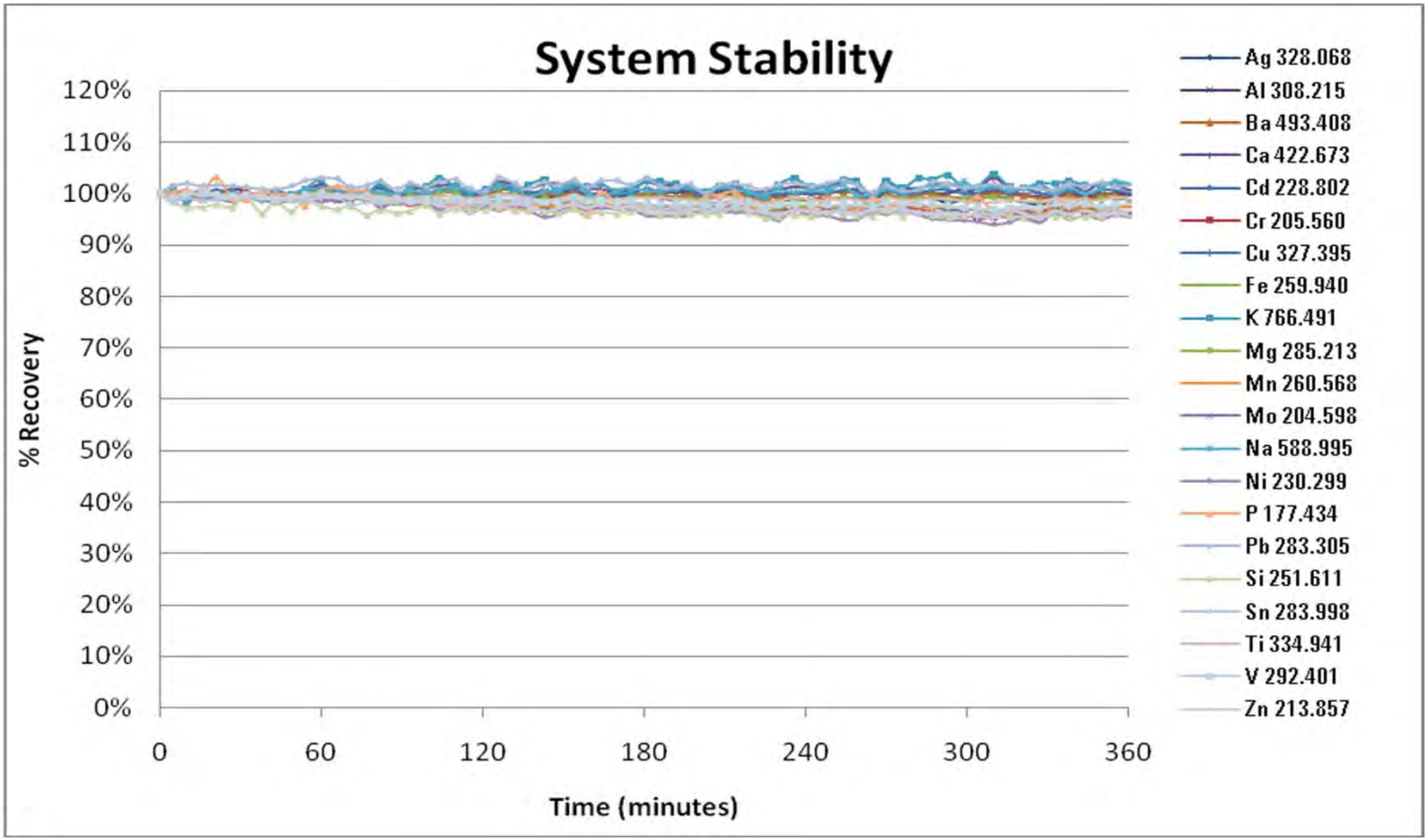
Element & wavelength	Certified (mg/kg)	Found (mg/kg)	Duplicate (mg/kg)	Recovery (%)	RPD dup. (%)	Spike level (mg/L)	Recovered (mg/L)	Recovery (%)
Ag 328.068	101.4	100.3	101.1	98.9	0.9	2.17	2.27	104.6
Al 308.215	(104)	99.7	100.4	95.9	0.7	2.17	2.27	104.3
Cr 205.560	98.3	104.3	105.5	106.1	1.2	2.17	2.27	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

Results
NIST SRM 1085b

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 & 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

Results
System stability



Experimental

Washout / carryover & speed of analysis

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

Speed of analysis

Tube-to-tube analysis time averaged 33 seconds, equating to > 100 samples/hour.

SVS 2 Results Summary

- Were able cut the sample analysis cycle time from about 90 seconds to about 33 seconds per sample using the SVS 2, without compromising accuracy, precision or stability.

- "Dead time" is eliminated (sample uptake, stabilization and washout times)

- SVS 2 utilizes stacked switching valves, sample loop and high speed, positive displacement motor

- *Constant solution flow improves plasma stability*

- *Sample never contacts pump tubing, inert sample path reduces sample carryover*

Application Papers

Available on the Agilent Technologies Web site (http://www.agilent.com)

- SI-A-1413 Determination of metals in oils by ICP-OES
- SI-A-1417 Determination of V, Ni and Fe in crude oils and bitumen with Sc as an internal standard
- SI-A-1420 Determination of wear metals in lubricating oil with Axial ICP
- SI-A-1422 Determination of Pb in Unleaded Gasoline with Axial ICP
- SI-A-1423 Determination of trace elements in a xylene solution of oil by ICP-AES with ultrasonic nebulization and membrane desolvation
- SI-A-1427 Multi-element analysis of fuel and lubricating oils by simultaneous ICP-OES
- SI-A-1431 Improving Throughput for Oils Analysis by ICP-OES

PLUS: SI-A-1202, SI-A-1415 and SI-A-1418

Questions?

THANK YOU