Abstract

Introduction
Improving productivity is a key issue for many laboratories that require fast, accurate and precise determinations of major, minor and trace elements in a variety of sample matrices. Achieving reliable improvements in sample throughput with ICP-OES can result in greater sample throughput capacity, improved laboratory responsiveness, or provide cost savings through reductions in argon consumption, labor, electricity and reagent consumption. We will evaluate a new sample introduction accessory for ICP-OES that uses flow-injection technology which is able to provide up to twice the sample throughput without compromising analytical accuracy or reproducibility. By eliminating the “dead time” in the sample introduction stages such as sample uptake, stabilization time and washout, it is possible to make significant gains in productivity without impinging on the actual measurement time.

In this work we will validate the system performance using a soil and plant tissue reference materials. This analysis is typical of those done in food and agriculture laboratories around the world.

This work describes the coupling of the SVS2, a new and innovative sample introduction system, with an Agilent 720 Series Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) to improve sample throughput. The SVS2 is comprised of a triple stacked 4-way diagonal flow switching valve, sample loop and a high speed, positive displacement pump. The SVS2 uses flow injection technology to virtually eliminate delays associated with sample uptake and pump stabilization.

A typical sample analysis cycle using and ICP-OES involves sample uptake at high pump rates from the autosampler to the plasma, followed by a stabilization delay to allow the plasma to come back into equilibrium, followed by a measurement of the sample before 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 about 1 minute. This equates to approximately 1440 solutions measured per day.

This SVS2 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. As a flow of solution to the plasma is constantly maintained, there is an improvement in plasma stability and reduction in stabilization times.

Experimental

Instrumentation
An Agilent 720 Series simultaneous ICP-OES with axially viewed plasma and SPFS autosampler was used for this work. The Agilent 720 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 that 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 SVS2 has two valve positions controlled in software. The first position (Figure 1) allows the sample to be quickly loaded into a sample loop by a positive displacement pump operating at up to 500 rpm. The size of the sample loop is dependant on the method, although a 0.5 mL can be filled in under 5 seconds. The sample is loaded and ready to be aspirated into the plasma for measurement.

When all of the sample is loaded in the injection loop, the controlling software triggers the valves to switch and inject the sample into the ICP-OES (Figure 2). In a typical analysis without the SVS2, sample is fast-pumped into the plasma destabilizing it, which results in a stabilization time of 10 to 15 seconds to settle prior to measurement. With the SVS2, sample is never directly injected into the plasma at high pump speeds ensuring much shorter stabilization delays can be used. In fact, an uptake delay isn’t required at all and a stabilization of <1s is sufficient to load the sample loop, inject the sample into the plasma to attain a stable signal. A system without SVS2 would typically require 20 seconds to perform the same function.

Results and Discussion

During the measurement phase the entire system is continuously flushed with rinse solution. Again, a conventional system without SVS2 would require a rinse time of at least 20 seconds to washout the system sufficiently to reduce the analyte signal to at least 4 orders of magnitude. With SVS2, the same level of washout is achievable without a rinse time saving a further 20 seconds.

A CEM Mars 5 closed-vessel microwave-assisted acid digestion system was used to extract the elements from the soil and leaf samples following USEPA method 3051A guidelines. This method is designed to mimic extraction using conventional heating with nitric acid (HNO3) and hydrochloric acid (HCl) and does not accomplish total decomposition and sample matrix compounds such as quartz, silicates, titanium dioxide, alumina and other oxides are not easily dissolved. Therefore, the extracted analyte concentrations may not reflect the total content in the sample. Internal standardization and ionization buffering was used throughout the analysis. A solution of 2 mg/L Ytrium (reference element) and 1% CsNO3 (ionization buffer) in a 5% HNO3 sample matched matrix was added online to the sample stream, using the third channel of the peristaltic pump, keeping sample preparation to a minimum.

Operating Parameters
- 1.3 kW RF Power
- 15 L/min Plasma gas flow
- 1.5 L/min Auxiliary gas flow
- Spray chamber type single pass glass crucible
- Torch Standard one piece quartz torch
- Nebulizer type Spray Ceramic Glass Nebulizer
- Nebulizer flow = 0.7 L/min

Pump tubing
- Rinse/instrument pump: white/white (1.02 mm ID)
- Waste: blue/blue (1.55 mm ID)
- Buffer/internal Standard: black/black (0.76 mm ID)

Pump speed = 12 rpm
- Total sample usage = 1 mL
- Replicate read time = 5 s
- Number of replications = 2
- Sample delay time = 0 s
- Stabilization time = 7 s
- Rinse time = 0 s
- Fast pump Off
- Fitted Background correction

SVS2 operating parameters
- 6 s Loop uptake delay
- 500 rpm uptake pump refill speed
- 100 rpm uptake pump inject speed
- 5 s Time in Sample
- 5 s Bubble Inject Time

Conclusions

Using the SVS2 with an Agilent 720 Series axially viewed ICP-OES the sample throughput cycle time is reduced from 60 seconds to less than 30 seconds while maintaining analytical accuracy and reducing cost of argon gas, standards and other reagents and longer lifetime of torches and pump tubing.

Washout between samples resulted in about 4 orders of magnitude in signal reduction.

Analytical stability was excellent.

With the swept volume of the SVS2 components minimized, sample throughput has been optimized and conveyer virtually eliminated.

As the sample does not make contact with peristaltic pump tubing prior to being aspirated into the plasma, the inert sample path results in reduced sample carry-over.

References
1. Calderon, V., Varian Application Note 35. Rapid measurement of major, minor and trace levels in soils using the Varian 730 ES
2. Ryan, A., Varian Application Note 33. Rapid measurement of major, minor and trace elements in plant and food material using the Varian 730 ES
3. USEPA Methods 3051A “Microwave assisted acid digestion of sediments, sludge and oils” Revision 1, January 1998

Table 1 Results for NIST SRM 2710 Montana soil digestion

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>Specified Range</th>
<th>Measured</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td>500-800</td>
<td>512 ± 38</td>
<td>90%</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg</td>
<td>30.6-400</td>
<td>315 ± 16</td>
<td>97%</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/kg</td>
<td>6.2-112</td>
<td>50 ± 0.70</td>
<td>115%</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>18</td>
<td>15.33 ± 1.5</td>
<td>99%</td>
</tr>
<tr>
<td>Ga</td>
<td>mg/kg</td>
<td>13.78-214.6</td>
<td>1033 ± 110</td>
<td>90%</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg</td>
<td>7.89 ± 0.22</td>
<td>90 ± 1.2</td>
<td>99%</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>4.036 ± 0.093</td>
<td>3.62 ± 0.28</td>
<td>89%</td>
</tr>
</tbody>
</table>

Table 2 Results for the NIST SRM 1571 orchard leaves

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>Specified Range</th>
<th>Measured</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>mg/kg</td>
<td>30-600</td>
<td>220.353 ± 0.96</td>
<td>94%</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td>2200-3300</td>
<td>2750 ± 0.09</td>
<td>90%</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg</td>
<td>37800-59000</td>
<td>5380 ± 0.09</td>
<td>90%</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>91.1</td>
<td>6.6 ± 0.15</td>
<td>99%</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td>15</td>
<td>15 ± 0.15</td>
<td>99%</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>900-1500</td>
<td>2300 ± 0.09</td>
<td>90%</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg</td>
<td>200-1500</td>
<td>3890 ± 0.09</td>
<td>90%</td>
</tr>
<tr>
<td>Sr</td>
<td>mg/kg</td>
<td>35-150</td>
<td>70 ± 0.15</td>
<td>99%</td>
</tr>
<tr>
<td>Sr</td>
<td>mg/kg</td>
<td>35-150</td>
<td>70 ± 0.15</td>
<td>99%</td>
</tr>
</tbody>
</table>

Figure 1 SVS2 in sample load position

Figure 2 SVS2 in sample inject position

Figure 3 1000 ppm Mn washout with and without SVS2

This information is subject to change without notice

D. Robbin and G. Russell, Agilent Technologies Australia Pty Ltd