Ultra-fast ICP-OES determinations of soil and plant material using next generation sample introduction technology

Application note

Agriculture

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Introduction

Testing soil for trace and major elements is the most important guide to the profitable and proper application of nutrients. This is critical to monitoring crop growth and assessing the potential for contamination of food crops. Plant tissue analysis is a complementary diagnostic tool that can help farmers with fertility management or assist them identify cost-effective ways to apply fertilizer and provide developing crops with additional nutrients, thereby reducing the chance of nutrient stress that may otherwise result in yield losses. There are ongoing demands for fast, accurate and precise determination of trace and major elements in agricultural samples such as soils and plant materials. With the capability to provide fast multi-element determinations over an extended range, simultaneous ICP-OES has become the most common technique for monitoring the health of soils and plant tissues in the agricultural industry. Laboratories completing these

determinations, whether government or private contract, all desire more productive analyses to handle growing sample workloads.

A typical sample analysis cycle involves sample uptake typically at higher pump rates, followed by a plasma stabilization delay, then measurement of the sample before washout of the sample from the sample introduction system. High throughput laboratories measuring large numbers of samples on a daily basis and working without any modification to the sample introduction system can typically measure a sample every minute. This equates to 1440 samples per day, excluding calibration and quality control standards, assuming continuous operation over 24 hours.

The biggest delays in the typical sample analysis are associated with sample introduction and washout. A sample introduction device based on use of a software controlled switching valve has demonstrated reduced analysis times from more efficient introduction and washout of sample from the sample introduction system[1]. This sophisticated device enables users to maximize the time spent on sample measurement and minimize the non productive time associated with sample introduction and washout.

This work describes the coupling of a new and innovative sample introduction system that uses flow injection technology combined with an Agilent 720 axially viewed Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). Termed the Switching Valve System 2 (or SVS 2) the sample introduction system comprises a software controlled, triple stacked four port diagonal flow switching valve, sample loop and a high speed, positive displacement pump.

Using the SVS 2, samples are loaded into the sample loop, ready for immediate analysis using the ICP-OES. In this manner, the SVS 2 improves the efficiency of sample introduction by greatly reducing sample uptake delays. Washout times are also reduced as the sample line is pre-emptively rinsed during the measurement cycle. Sample analysis times of less than 30 seconds per sample can be routinely achieved. This results in more than twice the sample throughput, reducing both total analysis time per sample batch, and analysis cost.

An additional benefit is that the flow of solution to the plasma is constant, improving plasma stability and thereby reducing stabilization times. 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.

The preparation and analysis of certified reference soil and plant materials as described in previous application papers[1,2] was repeated using the SVS 2 to illustrate the throughput advantage of the device.

A microwave-assisted acid digestion, based on recommendations given in US EPA Method 3051A3 was used to rapidly extract the elements from the soil and plant samples. This method is not intended to accomplish total sample decomposition. For many environmental monitoring purposes, the concentrations of extractable elements are more important than total concentrations, as bound elements are not considered mobile in the environment.

Using the SVS 2, the sample to sample cycle time is reduced to less than 30 seconds whilst maintaining analytical accuracy and reducing cost of argon gas and consumables usage — longer lifetime of torches and pump tubing, reduced usage of acids, standards and other chemicals.

Experimental

Instrumentation

An Agilent 720 simultaneous ICP-OES with axially viewed plasma was used for the analysis.

The Agilent 720 ICP-OES features a custom designed CCD detector which provides true simultaneous measurement, full wavelength coverage from 167 to 785 nm and fast read-out enabling short sample analysis times. The CCD detector has pixels arranged in continuous angled arrays that are matched exactly to the two-dimensional image from the Echelle polychromator. The optical system is housed within a thermally stabilized environment at 35 °C and contains no moving parts, ensuring excellent long-term stability. The polychromator can be purged with either argon or nitrogen gas for improved performance when measuring at low UV wavelengths.

The system is available with a choice of sample introduction system; either a three- or four-channel peristaltic pump for sample introduction and mass flow control or manual pressure control of the nebulizer gas flow. For this application, the system was fitted with a mass flow controller and a four-channel peristaltic pump. The four-channel peristaltic pump allows the sample, internal standard/ionization buffer solution, rinse solution and the waste to be simultaneously pumped.

A conventional one-piece axial torch was used. The sample introduction system consisted of a concentric glass nebulizer and a glass cyclonic chamber. Agilent ICP Expert II software was used for instrument operation.

The SVS 2 accessory (Figure 1) brings a new concept to the sample introduction system of ICP-OES systems. The SVS 2 utilizes two, software triggered, valve positions.

Figure 1. The Agilent SVS 2 accessory

The first position allows the sample to be quickly loaded into a sample loop using the high speed positive displacement pump (Figure 2). The size of the sample loop is dependent on the method. The positive displacement pump can operate at up to 500 rpm, enabling loading of the sample loop; for example, a 0.5 mL sample loop can be filled in under five seconds. Whilst the sample loop is being filled, the sample introduction system is rinsed with a combined flow of rinse solution and internal standard. The continuous aspiration of solution to the plasma improves plasma stability and reduces stabilization times. Once the sample loop has been filled, the sample is ready to be aspirated through the nebulizer into the plasma for measurement.

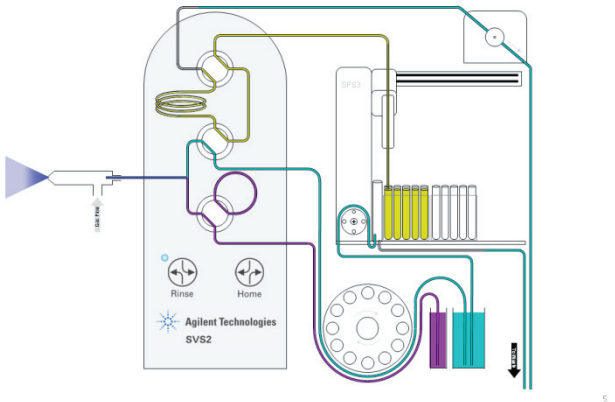

Figure 2. In the first valve position (Fill), the sample loop is filled with sample solution using the high speed, positive displacement pump. During this fill step, rinse and internal standard is aspirated through the nebulizer.

The controlling software triggers the valve to switch so that the sample is pumped through the nebulizer with the flow of internal standard (Figure 3). At the same time, the autosampler probe and sample uptake tubing are rinsed using rinse solution pumped with the positive displacement pump. Note that the sample does not contact the peristaltic pump tubing at any time, reducing carry-over.

In a typical ICP-OES analysis without the SVS, sample is fast-pumped into the plasma, and the pump speed is then reduced to normal speed for the duration of the measurement. The change from high to low sample flow destabilizes the plasma and may result in an unstable signal for a short period. To allow the plasma to re-equilibrate at the normal pump speed, a stabilization

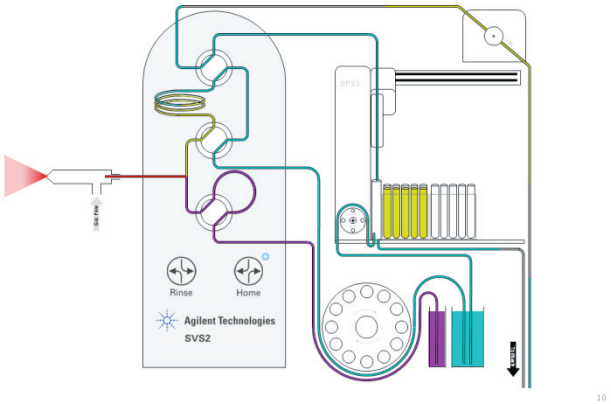

Figure 3. In the second valve position (Inject), the rinse solution pushes the sample towards the nebulizer, where it is combined with the internal standard prior to measurement using the ICP-OES. During this inject step, the autosampler probe and sample uptake tubing are rinsed by the positive displacement pump.

time of 10–15 seconds is required to enable the signal to stabilize prior to measurement. Using the SVS 2, the flow of solution into the plasma remains constant. High pump speeds are used to fill the sample loop, but the sample loop is disconnected from the plasma during this step. The continuous flow of solution through the nebulizer ensures better plasma stability and allows much shorter stabilization delays to be used. In addition, an uptake delay is not required. A stabilization time of <10 s is sufficient to load the sample loop and inject the sample into the plasma to attain a stable signal. Conventional ICP-OES systems operating without the SVS 2 would typically require an additional 25 seconds to perform the same function.

Another benefit of the SVS 2 is that it continuously flushs the entire system with rinse solution. Conventional ICP-OES systems using an autosampler for sample presentation typically require an extended rinse time of at least 20 seconds to ensure sufficient washout of the sample introduction system, which means the analyte signal is reduced by at least four orders of magnitude. Using the SVS 2, the same level of washout is achievable without needing to program a separate rinse time into the method parameters, leading to a further 20 second reduction in analysis time.

The reference element technique (internal standardization) and ionization buffering were used throughout the analysis. Internal standardization allows

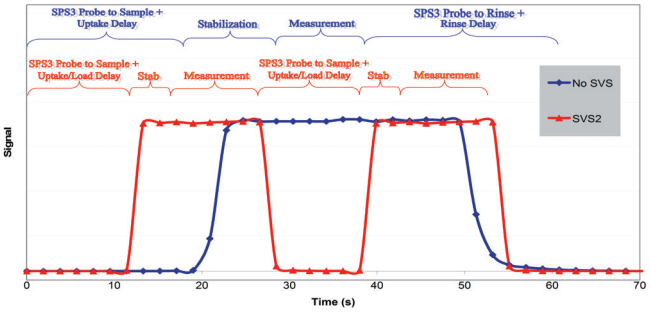

Figure 4. Compare the analysis profiles for determination of 100 mg/L manganese using ICP-OES. Using the SVS 2 (red profile), two samples can be measured in the time required to measure a single sample when using a conventional ICP-OES system without the SVS 2 (blue profile).

correction for physical differences that may exist between sample types. Ionization buffering greatly minimizes the effects of ionization interferences that can result from the presence of high levels of easily ionized elements (EIE) such as sodium, potassium and calcium that potentially exist with such matrix types. A solution containing 2 mg/L yttrium (reference element) and 1% caesium nitrate (ionization buffer) prepared in a 5% nitric acid matrix (matched to the sample) was added on-line to the sample stream, using the third channel of the peristaltic pump. With on-line addition of the internal standard and ionization buffer, sample preparation is kept to a minimum. Otherwise, all standard, QC solutions and samples must be prepared in a matrix of 2 mg/L yttrium (reference element) and 1% caesium nitrate (ionization buffer).

A Mars 5 closed-vessel, microwave digestion system from CEM Corporation was used to digest the solid samples. The Mars 5 is a microwave laboratory workstation designed to make sample preparation quick and easy. The system comes equipped with internal temperature and pressure as a standard feature, which is critical for safety. In addition the system uses Reactiguard to monitor pressure relief in any of the vessels.

An external temperature device can be added to the system to measure and record the temperatures in order to provide a measure of safety when working with high temperature digestions. Up to 12 samples can be safely processed using XP 1500 Plus vessels for fast, complete and reproducible digestions.

Solutions were automatically presented to the spectrometer using the Agilent SPS 3 Sample Preparation System, under control of the operating software. Tables 1 and 2 list the operating conditions used for the ICP-OES and the SVS 2 during this analysis.

Table 1. ICP-OES instrument operating parameters

Condition	Setting
Power	1.3 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Glass cyclonic (single-pass)
Torch	Standard one piece quartz axial
Nebulizer type	SeaSpray
Nebulizer flow	0.7 L/min
Pump tubing	Rinse/Instrument pump: white-white tabs (1.02 mm id) Waste: blue-blue tabs (1.65 mm id) Ionization buffer/Internal standard: black-black tabs (0.76 mm id)
Pump speed	12 rpm
Total sample usage	1 mL
Replicate read time	5 s
Number of replicates	2
Sample uptake delay time	0 s
Stabilization time	7 s
Rinse time	0 s
Fast pump	Off
Background correction	Fitted

Table 2. SVS 2 operating parameters

Condition	Setting
Loop uptake delay	6 s
Uptake pump speed — refill	500 rpm
Uptake pump speed — inject	93 rpm
Sample loop size	0.5 mL
Time in sample	5 s
Bubble inject time	5 s

Preparation of calibration solutions

Calibration solutions were prepared from custom-grade multi-element solutions VAR MAJOR 1A and VAR CAL 3, supplied by Inorganic Ventures Inc. These solutions contained the following elements at the nominated concentrations:

- VAR-MAJOR-1A (5000 mg/L): Ca, Fe, K, Mg, and Na
- VAR-CAL-3 (1000 mg/L): Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Th, Tl, U, V and Zn

The calibration standards and calibration blank solutions were prepared in > 18 MΩ•cm deionized water supplied from a Millipore system and stabilized with 5% v/v HNO_3 (Merck Tracepur). The reference element/ionization buffer solution containing 2 mg/L yttrium and 1% w/v caesium nitrate was prepared from Spex CertiPrep single element solution of 1000 mg/Lyttrium, and Sigma Aldrich caesium nitrate (99.999% purity) prepared in a matrix of 5% v/v HNO_3 (Merck Tracepur).

Tables 3 and 4 list the selected elemental wavelengths and concentration range covered by the calibration standards for each element. Sensitivity, linear dynamic range and freedom from spectral interferences were taken into consideration during wavelength selection.

Table 3. Element wavelength and calibration range selected for the minor and trace elements (mg/L)

Element	Wavelength (nm)	Std 1	Std 2	Std 3	Std 4
Al	396.152	0.1	1	10	50
As	188.980	0.1	1	10	50
Ba	455.403	0.1	1	10	50
Cd	226.502	0.1	1	10	50
Co	228.615	0.1	1	10	50
Cr	267.716	0.1	1	10	50
Cu	324.754	0.1	1	10	50
Mn	257.610	0.1	1	10	50
Ni	231.604	0.1	1	10	50
Pb	220.353	0.1	1	10	50
V	292.401	0.1	1	10	50
Zn	206.200	0.1	1	10	50

Table 4. Element wavelength and calibration range selected for the major elements (mg/L)

Element	Wavelength (nm)	Std 5	Std 6	Std 7	Std 8
Ca	315.887	1	10	100	250
Fe	234.350	1	10	100	250
K	766.491	1	10	100	250
Mg	285.213	1	10	100	250
Na	588.995	1	10	100	250

Sample preparation

The CEM Mars 5 closed-vessel microwave-assisted digestion system was used to extract the elements from the soil and leaf samples. The digestion procedure was based upon recommendations in US EPA method 3051A guidelines.[3] This microwave extraction method is designed to mimic extraction using conventional heating with nitric acid (HNO_3) and hydrochloric acid (HCl). This method is not intended to accomplish total sample decomposition, and sample matrix compounds such as quartz, silicates, titanium dioxide, alumina and other oxides are not easily dissolved. Total decomposition of the sample may not necessarily occur. Therefore, the measured analyte concentrations may not reflect the total content in the sample.[4]

Two certified reference materials from the National Institute of Standards and Technology (NIST) were used to validate the method (SRM 2710 Montana Soil and SRM 1571 Orchard Leaves).

The soil and leaf samples were prepared by accurately weighing 0.5 g of sample into the microwave digestion vessels and adding 9 mL of 10 M HNO_3 (Merck Tracepur) and 3 mL of 10 M HCl (AnalaR). The vessels were capped and placed in the microwave digestion system.

Tables 5 and 6 list the settings used for the temperature dependent, microwave assisted digestion.

Following digestion, the solutions were cooled, then centrifuged for 30 minutes and transferred to 50 mL volumetric flasks. Each solution was diluted to volume with >18 MΩ•cm deionized water. Duplicate digestions were carried out.

Table 5. Settings used for microwave digestion of soil samples

Stage	Max. power (W)	% power	Ramp (min)	Pressure (psi)	Temp. (°C)	Hold (min)
1	600	100	5:00	350	120	0:00
2	600	100	5:30	350	175	4:30

Table 6. Settings used for microwave digestion of leaf samples

Stage	Max. power (W)	% power	Ramp (min)	Pressure (psi)	Temp. (°C)	Hold (min)
1	600 W	100	3:00	350	120	5:00
2	600 W	100	10:00	350	200	10:00

For both microwave digestion procedures, Stage 1 was added as a reflux step to enable removal of any particulate matter that had adhered to the walls of the microwave vessel during sample addition.

The moisture content of each reference material (Table 7) is required as the certified values are based on dry weights. The data was adjusted accordingly.

Table 7. Moisture content

	Quoted average moisture content
Montana Soil (NIST SRM 2710)	2.0%
Orchard Leaves (NIST SRM 1571)	3.1%

Results and discussion

The measured concentrations of major, minor and trace elements in the respective soil and plant reference materials are reported in Tables 8 and 9 (see Appendix). Digestions were performed in duplicate and analyses were performed in triplicate and averaged. The error reported for each result represents the largest variation from the mean value.

Although a small amount of undissolved material was observed following microwave digestion, the overall measured concentrations of extractable major, minor and trace elements in the soil samples were in good agreement with the certified leach data and consistent with similar work reported in the past.[1,2]

Conclusion

Two certified reference materials containing widely varied levels of major, minor and trace elements were digested using a microwave assisted extraction method following US EPA Method 3051A. The sample digests were determined using an Agilent 720 axially-viewed simultaneous ICP-OES equipped with an innovative sample introduction system that uses flow injection technology (SVS 2). The use of the SVS 2 sample introduction system resulted in significantly increased sample throughput, with a sample to sample duration of 30 seconds.

References

1. A. Ryan, Rapid measurement of major, minor and trace elements in plant and food material using the Agilent 730 ICP-OES.

2. V. Calderon, Rapid measurement of major, minor and trace levels in soils using the Agilent 730 ICP-OES.

3. United States Environmental Protection Agency (US EPA) Method 3051A "Microwave assisted acid digestion of sediments, sludge and oils" Revision 1, January 1998.

4. CEM Microwave sample preparation Notes (Mars 5).

Appendix

Although a small amount of undissolved material was observed following microwave digestion, the overall measured concentrations of extractable major, minor and trace elements in the soil samples were in good agreement with the certified leach data and consistent with similar work reported in the past.[1,2]

One exception was the achieved recoveries for Na in NIST SRM 2710 Montana Soil (128% and 128% for the original sample and duplicate, respectively), suggesting the likelihood of contamination in the original sample. While the results for Co in this sample also show an elevated recovery (compared with the reference data for the leachable concentration), they compare well with the non certified or reference value quoted of 10 mg/kg, yielding recoveries of 96.7 % for digestion 1 and 98.5 % for digestion 2. This suggests that the microwave extraction method used is recovering all of the Co from the sample. It is also noted that the digestion used to determine the reference data for the leachable Co was based on less aggressive hot plate digestion using nitric acid and hydrogen peroxide. This can also account for the differences in the reported recoveries for the Co in NIST SRM 2710 Montana Soil.

Table 8. Measured results for the extractable major, minor and trace elements in NIST SRM 2710 Montana Soil

	Al (Wt%)	Ca (Wt%)	Fe (Wt%)	Mg (Wt%)	K (Wt%)	Na (Wt%)	Zn (mg/kg)	Mn (mg/kg)	Cu (mg/kg)
Reference data (leachable concentrations)									
Median	1.8	0.41	2.7	0.57	0.45	0.054	5900	7700	2700
Range	1.2–2.6	0.38–0.48	2.2–3.2	0.43–0.60	0.37–0.50	0.049–0.062	5200–6900	6200–9000	2400–3400
Sample data									
Digestion 1	1.87 ± 0.18	0.40 ± 0.02	3.14 ± 0.35	0.54 ± 0.02	0.50 ± 0.02	0.069 ± 0.004	5476 ± 424	6937 ± 615	2510 ± 128
Recovery	104	98	117	95	112	128	93	90	93
Duplicate data									
Digestion 2	1.95 ± 0.18	0.39 ± 0.02	3.18 ± 0.41	0.52 ± 0.02	0.52 ± 0.02	0.069 ± 0.004	5479 ± 430	6914 ± 655	2523 ± 143
Recovery	109	94	118	92	115	128	93	90	93
	Ba (mg/kg)	**Pb (mg/kg)**	**As (mg/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**Co (mg/kg)**	**Cd (mg/kg)**	**V (mg/kg)**	**Cu (mg/kg)**
Reference data (leachable concentrations)									
Median	360	5100	590	19	10.1	8.2	20	43	2700
Range	300–400	4300–7000	490–600	15–23	8.8–15	6.3–12	13–26	37–50	2400–3400
Sample data									
Digestion 1	317.7 ± 9.1	4576 ± 293	538 ± 36	18.7 ± 1.5	10.0 ± 1.2	9.66 ± 0.79	19.7 ± 1.1	44.9 ± 3.5	2510 ± 128
Recovery	88	90	91	99	99	118	98	104	93
Duplicate data									
Digestion 2	317.7 ± 13.9	4592 ± 312	539 ± 39	19.2 ± 1.5	10.1 ± 0.9	9.85 ± 0.91	19.8 ± 1.3	46.1 ± 3.4	2523 ± 143
Recovery	88	90	91	101	100	120	99	107	93

Table 9. Measured results for the extractable major, minor and trace elements in NIST SRM 1571 Orchard Leaves.
Values shown in parentheses are reference values only (not certified).

	Al (µg/g)	Ca (Wt%)	Fe (µg/g)	Mg (Wt%)	K (Wt%)	Na (µg/g)	Zn (µg/g)	Mn (µg/g)	Cu (µg/g)
					Reference data				
Certified median	N/A	2.09	300	0.62	1.47	82	25	91	12
Certified range	—	2.06–2.12	280–320	0.60–0.64	1.44–1.50	76–88	22–28	87–95	11–13
					Sample data				
Digestion 1	269 ± 6	2.29 ± 0.05	282.8 ± 3.4	0.60 ± 0.01	1.45 ± 0.10	66.8 ± 0.9	26.8 ± 0.6	91.7 ± 0.8	12.0 ± 0.7
Recovery	—	109	94	96	99	81	107	101	100
					Duplicate data				
Digestion 2	242 ± 11	2.27 ± 0.03	277.1 ± 3.1	0.59 ± 0.02	1.42 ± 0.11	59.3 ± 1.4	24.6 ± 1.9	92.3 ± 1.6	11.8 ± 0.6
Recovery	—	108	92	94	97	72	98	101	98
	Ba (µg/g)	**Pb (µg/g)**	**As (µg/g)**	**Cr (µg/g)**	**Ni (µg/g)**	**Co (µg/g)**	**Cd (µg/g)**	**V (mg/kg)**	
					Reference data				
Certified median	(44)	45	10	2.6	1.3	(0.2)	0.11	N/A	
Certified range	—	42–48	8–12	2.3–2.9	1.1–1.5	—	0.10–0.12	—	
					Sample data				
Digestion 1	43.1 ± 1.1	42.1 ± 1.8	10.4 ± 0.6	2.55 ± 0.15	1.44 ± 0.02	0.10 ± 0.05	0.11 ± 0.02	0.37 ± 0.02	
Recovery	98	94	104	98	111	49	104	—	
					Duplicate data				
Digestion 2	42.0 ± 1.3	42.3 ± 1.6	10.4 ± 0.4	2.55 ± 0.15	1.34 ± 0.16	0.16 ± 0.04	0.10 ± 0.01	0.32 ± 0.03	
Recovery	95	94	103	98	103	80	93	—	

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