Rapid Measurement of Major, Minor and Trace Levels in Soils Using the Agilent 730-ES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

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Introduction

As part of the global strategy for sustainable farming, considerable emphasis has been placed on the need for fast, accurate and precise determination of elements in agricultural soil. As a result, simultaneous ICP-OES has become a widely used technique for reporting the health of soils in the agricultural industry.

This work describes the preparation and analysis of certified reference soil materials using the Agilent 730-ES simultaneous ICP-OES with CCD detection. The Agilent 730-ES includes a switching valve system that improves the efficiency of sample introduction and washout, providing greater sample throughput and accuracy.

A microwave-assisted acid digestion, based on recommendations given in US EPA method 3051A, was used to rapidly extract the elements from the soil samples. 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. 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 [1].

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Instrumentation

An Agilent 730-ES (simultaneous ICP-OES with axially viewed plasma) was used for the analysis.

The Agilent 730-ES 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 Agilent 730-ES also includes the productivity-enhancing Switching Valve System (SVS) that provides more efficient sample introduction and washout than traditional sample introduction systems. The SVS consists of a software-controlled, 4-port switching valve that instantaneously rinses the spray chamber following sample measurement while simultaneously presenting the next sample for measurement.

A Mars % closed vessel, microwave digestion system from CEM was used to digest the solid samples.

Solutions were presented to the spectrometer using the Agilent SPS3, Sample Preparation System.

Table 1 shows the operating parameters used in this work.

Table 1. Operating Parameters

Condition	Setting
Power	1.2 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Glass cyclonic (single-pass)
Torch	Standard axial torch
Nebulizer type	Seaspray
Nebulizer flow	0.7 L/min
Pump tubing	Sample: white-white (1.02 mm ID) Waste: blue-blue (1.65 mm ID) Buffer/Reference element: black-black (0.76 mm id)
Pump speed	15 rpm
Total sample usage	1 mL
Replicate read time	3 s
Number of replicates	3
Sample delay time	20 s
Switching valve delay	17 s
Stabilization time	12 s
Rinse time	1 s
Fast pump	On
Background correction	Fitted

Preparation of Calibration Solutions

Calibration solutions were prepared from Inorganic Ventures Inc. custom-grade multi-element solutions (VAR-CAL-1A, VAR-CAL-2A and VAR-MAJOR-1A) and from Spex CertiPrep single element solutions. These solutions contained the following elements:

VAR-CAL-1A (1000 mg/L): Mo, Sb, Sn, and Ti

VAR-CAL-2A (1000 mg/L): Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Th, Tl, U, V, and Zn

VAR-MAJOR-1A (5000 ng/L): Ca, Fe, K, Mg, and Na

Spex CertiPrep single element solutions: 1000 mg/L Al
1000 mg/L P
1000 mg/L Sr
1000 mg/L Ti

Tables 2 and 3 list the selected elemental wavelengths and standard concentrations used to calibrate each element. Sensitivity, linear dynamic range and freedom from spectral interferences were taken into consideration during wavelength selection.

Table 2. Calibration Standards for the Major and Minor Elements

Element	Wavelength (nm)	Std 1 (mg/L)	Std2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	Std 5 (mg/L)	Std 6 (mg/L)
Al	396.125	2	10	20	100	200	500
Ca	317.933	1	10	20	100	200	500
Fe	234.350	1	10	20	100	200	500
Mg	285.213	1	10	20	100	200	-
K	766.491	1	10	20	100	–	–
P	178.222	1	10	20	–	–	–
Na	588.995	1	10	20	–	–	–
Ti	336.122	1	10	20	–	–	–

Table 3. Calibration Standards for the Minor and Trace Elements

Element	Wavelength (nm)	Std 1 (µg/L)	Std2 (µg/L)	Std 3 (µg/L)	Std 4 (µg/L)	Std 5 (µg/L)	Std 6 (µg/L)
Cu	327.395	10	50	250	1000	10 000	100 000
Pb	220.353	10	50	250	1000	10 000	100 000
Mn	260.568	10	50	250	1000	10 000	100 000
Zn	206.200	10	50	250	1000	10 000	100 000
As	188.980	10	50	250	1000	10 000	–
Ba	455.403	10	50	250	1000	10 000	–
Cr	267.716	10	50	250	1000	10 000	–
Sr	407.771	20	50	250	1000	10 000	–
Ni	231.604	10	50	250	1000	–	–
V	292.401	10	50	250	1000	–	–
Cd	226.502	10	50	250	–	–	–

The calibration standard and blank solutions were prepared in > 18MΩ/cm^3 deionized water supplied from a Millipore system and stabilized with 5% v/v HNO_3 (Merck Tracepur).

A solution containing 2 mg/L yttrium and 1% w/v $CsNO_3$ in 5% v/v Tracepur HNO_3 was introduced to the sample online via the third channel of the peristaltic pump. Yttrium was used for reference element (internal standard) correction and cesium was used as an ionization buffer to eliminate ionization affects that potentially exist with such matrix types [2-3].

Sample Preparation

A closed-vessel microwave-assisted acid digestion was used to extract the major, minor and trace elements from the soil samples following USEPA method 3051A guidelines. This method is designed to mimic extraction using conventional heating with nitric acid (HNO_3) and hydrochloric acid (HCl) and does not accomplish total decomposition of the sample. Therefore, the extracted analyte concentrations may not reflect the total content in the sample [4]. Certified reference materials NIST SRM 2710 Montana Soil and NIST SRM 2709 San Joaquin Soil were used to validate the method.

The soil samples were prepared by accurately weighing 0.25 g of sample into the microwave digestion vessels and adding 9 mL of 10M HNO_3 (Merck Tracepur) and 3 mL of 10 M HCl (AnalaR). Following digestion, the solutions were cooled, then centrifuged for 30 minutes and transferred to 25.00 mL volumetric flasks. Each solution was diluted to volume with >18MΩ/cm^3 deionized water. Duplicate digestions were carried out.

Table 4 shows the settings used for the temperature dependent, microwave assisted digestion.

Table 4. Settings Required for Microwave Digestion

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

Stage 1 was added as a reflux step to remove particulate matter that adhered to the walls of the microwave vessel during sample addition.

The moisture content of each reference material was determined as the certified values are based on dry weights. The samples were oven dried at 110 °C for 2 hours then cooled in a desiccator for 4 hours. The data were adjusted accordingly.

Table 5. Moisture Content

	Measured moisture content	Quoted moisture content range
Montana soil (NIST SRM 2710)	2.3%	1.7%–2.3%
San Joaquin soil (NIST SRM 2709)	2.4%	1.8%– 2.5%

Results and Discussion

The measured concentrations of major, minor and trace elements in the respective soil reference materials are reported in Tables 6–10. Analyses were performed in triplicate and the error reported for each result represents the largest variation from the mean value.

Table 6. Extractable Major Elements in Soil

		Al (Wt%)	Ca (Wt%)	Fe (Wt%)	Mg (Wt%)
NIST SRM 2710 Montana soil	**Reference data**				
	Certified median	1.8	0.41	2.7	0.57
	Certified range	1.2–2.6	0.38–0.48	2.2–3.2	0.43–0.60
	Sample data				
	Digestion 1	2.07 ± 0.01	0.376 ± 0.003	2.50 ± 0.03	0.510 ± 0.016
	Recovery	115	92	93	89
	Duplicate data				
	Digestion 2	2.05 ± 0.004	0.377 ± 0.001	2.50 ± 0.001	0.508 ± 0.005
	Recovery	114	92	93	89
NIST SRM 2709 San Joaquin soil	**Reference data**				
	Certified median	2.6	1.5	3.0	1.4
	Certified range	2.0–3.1	1.4–1.7	2.5–3.3	1.2–1.5
	Sample data				
	Digestion 1	2.00 ± 0.01	1.38 ± 0.01	2.63 ± 0.01	1.15 ± 0.01
	Recovery	77	92	88	82
	Duplicate data				
	Digestion 2	2.54 ± 0.02	1.38 ± 0.01	2.74 ± 0.01	1.21 ± 0.02
	Recovery	98	92	91	86

Table 7. Extractable Major and Minor Elements in Soil

		K (Wt%)	P (Wt%)	Na (Wt%)	Ti (Wt%)
NIST SRM 2710 Montana soil	**Reference data**				
	Certified median	0.45	0.11	0.054	0.10
	Certified range	0.37–0.50	0.106–0.11	0.049–0.062	0.092–0.11
	Sample data				
	Digestion 1	0.497 ± 0.003	0.0677 ± 0.0008	0.0613 ± 0.0003	0.122 ± 0.001
	Recovery	110	62	114	122
	Duplicate data				
	Digestion 2	0.492 ± 0.001	0.0681 ± 0.0001	0.0612 ± 0.0002	0.120 ± 0.0003
	Recovery	109	62	113	120
NIST SRM 2709 San Joaquin soil	**Reference data**				
	Certified median	0.32	0.07	0.068	0.038
	Certified range	0.26–0.37	0.05–0.07	0.063–0.11	0.03–0.04
	Sample data				
	Digestion 1	0.347 ± 0.001	0.0442 ± 0.0003	0.0636 ± 0.0005	0.0234 ± 0.0001
	Recovery	108	63	94	62
	Duplicate data				
	Digestion 2	0.408 ± 0.004	0.0444 ± 0.0004	0.0684 ± 0.0003	0.0545 ± 0.0006
	Recovery	127	63	101	143

Table 8. Extractable Major and Minor Elements in Soil

		Zn (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Ba (mg/kg)	Sr (mg/kg)
NIST SRM 2710 Montana soil	**Reference data**					
	Certified median	5900	7700	2700	360	100
	Certified range	5200–6900	6200–9000	2400–3400	300–400	94–110
	Sample data					
	Digestion 1	5815 ± 46	7054 ± 86	2426 ± 20	307 ± 4	90.9 ± 1.1
	Recovery	99	92	90	85	91
	Duplicate data					
	Digestion 2	5897 ± 18	7064 ± 10	2436 ± 5	306 ± 1	90.6 ± 0.2
	Recovery	100	92	90	85	91
NIST SRM 2709 San Joaquin soil	**Reference data**					
	Certified median	100	470	32	398	101
	Certified range	87–120	360–600	26–40	392–400	100–112
	Sample data					
	Digestion 1	87.2 ± 0.3	483 ± 3	29.2 ± 0.3	367 ± 1	88.7 ± 0.5
	Recovery	87	103	91	92	88
	Duplicate data					
	Digestion 2	84.2 ± 0.6	485 ± 6	29.3 ± 0.1	377 ± 3	91.4 ± 0.3
	Recovery	84	103	92	95	90

Table 9. Extractable Major, Minor and Trace Elements in Soil

		Pb (mg/kg)	As (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Co (mg/kg)
NIST SRM 2710 Montana soil	**Reference data**					
	Certified median	5100	590	19	10.1	8.2
	Certified range	4300–7000	490–600	15–23	8.8–15	6.3–12
	Sample data					
	Digestion 1	4433 ± 22	514 ± 4	19.3 ± 0.1	10.4 ± 0.1	8.90 ± 0.06
	Recovery	87	87	102	103	109
	Duplicate data					
	Digestion 2	4484 ± 29	518 ± 1	19.2 ± 0.1	10.3 ± 0.2	8.99 ± 0.05
	Recovery	88	88	101	102	110
NIST SRM 2709 San Joaquin soil	**Reference data**					
	Certified Median median		13	< 20	79	78 12
	Certified Rangerange	12–18	–	60–115	65–90	10–15
	Sample data					
	Digestion 1	10.7 ± 0.1	15.3 ± 0.1	61.8 ± 0.2	67.7 ± 0.6	11.1 ± 0.1
	Recovery	82	–	78	87	93
	Duplicate data					
	Digestion 2	11.0 ± 0.5	15.2 ± 0.6	72.5 ± 0.2	68.2 ± 0.3	11.5 ± 0.1
	Recovery	85	–	92	87	96

Table 10. Extractable Major, Minor and Ttrace Elements in Soil

		Cd (mg/kg)	Mo (mg/kg)	V (mg/kg)
NIST SRM 2710 Montana soil	**Reference data**			
	Certified median	20	20	43
	Certified range	13–26	13–27	37–50
	Sample data			
	Digestion 1	16.4 ± 0.1	14.94 ± 0.1	48.74 ± 0.5
	Recovery	82	75	113
	Duplicate data			
	Digestion 2	16.64 ± 0.1	14.4 ± 0.3	48.64 ± 0.1
	Recovery	83	75	113
NIST SRM 2709 San Joaquin soil	**Reference data**			
	Certified Median median	< 1	< 2	62
	Certified Rangerange	–	–	51–70
	Sample data			
	Digestion 1	< 0.2	1.514 ± 0.03	60.04 ± 0.2
	Recovery	–	–	97
	Duplicate data			
	Digestion 2	< 0.4	1.494 ± 0.05	74.24 ± 0.2
	Recovery	–	–	120

Note: < value indicates an undetected element with the < value expressed as 10 times the standard deviation of background emission.

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.

The major and minor elements Al, Fe, Mg, Na and K were within 15% of the respective certified median values and within the certified range for Montana soil (NIST SRM 2710). The same can be said for San Joaquin soil (NIST SRM 2709) although variation between the original (digestion 1) and duplicate values (digestion 2) were found to be greater with the measured value for magnesium in the original sample and potassium in the duplicate falling just outside the certified range. Good recovery was also achieved for calcium at 92% for both soil samples and duplicates, although the measured concentrations fell just outside the lower end of the certified range. With a measured recovery of 62–63% in both soil sample types, phosphorus did not appear to undergo complete extraction, although the reproducibility of the extraction for P was excellent. On the other hand, titanium produced mixed results suggesting incomplete extraction and in homogeneity.

The majority of the remaining extractable major, minor and trace elements (Zn, Mn, Cu, Ba, Sr, Pb, As, Cr, Ni, Cd, Co, Mo and V) fell within the certified range. Those that did not fall within the certified ranges were within 16% of the certified median value.

Conclusion

Two certified reference soil materials, containing variable levels of major, minor and trace elements were digested following US EPA Method 3051A and analysed on the Agilent 730-ES Simultaneous ICP-OES. Agreement between the measured and certified values was generally very good.

The switching valve, fast rinse accessory was also used allowing more efficient introduction and washout of the sample from the sample introduction system. The determination of 21 elements in a sample took less than 65 seconds and required approximately 1 mL of solution, making the Agilent 730-ES an excellent analytical tool for fast and efficient analysis of soils.

References

A. Ryan, “Direct analysis of milk powder on the Liberty Series II ICP-AES with the axially-viewed plasma”. ICP Instruments at work, **1997**, ICP-21.

US EPA Method 3051A “Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils”. Revision 1, **1998**.

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