

Determination of elemental nutrients in DTPA extracted soil using the Agilent 5110 SVDV ICP-OES

Application note

Food safety and Agriculture

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Introduction

The elemental content of soils can impact plant development and crop yields as well as the safety of plant-based produce. Consequently, soil testing of micronutrients is commonly conducted to assess soil fertility, while heavy metals are analyzed to identify any potential toxicity issues.

Depending on the elements of interest in soils, different extraction methods and analytical techniques are employed. Soil extracting solutions containing chelating agents such as diethylenetriaminepentaacetic acid (DTPA) are often used for the extraction of micronutrients.

The extracted solutions are commonly analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) because the technique provides low cost of analysis and the wide concentration ranges required for soil testing, making it ideal for high throughput agricultural labs.

Radial View (RV) ICP-OES instruments are typically used for the analysis of agricultural samples due to the robustness of the vertical torch. However, sensitivity is compromised leading to higher detection limits. In contrast, the Agilent 5110 Synchronous Vertical Dual View (SVDV) ICP-OES features an axially-viewed, vertically-oriented plasma. This is ideal for complex agricultural samples such as soils, as SVDV ICP-OES provides much lower detection limits than RV ICP-OES.

The Agilent 5110 SVDV ICP-OES provides:

- **Stability:** the 5110's solid state radio frequency (SSRF) system operates at 27 MHz, providing a robust and stable plasma capable of handling a wide range of samples, including complex matrices such as DTPA. The SSRF adjusts to rapid changes in the plasma, even when the sample uptake speed is increased via fast pumping to 80 rpm. This allows the same plasma gas flow rate to be used, regardless of sample type, accelerating method development by simplifying analytical parameter settings.
- **Simplicity:** the intuitive Agilent ICP Expert software has a familiar worksheet interface for easy method development.
- **Speed and performance:** SVDV with Dichroic Spectral Combiner (DSC) technology captures the axial and radial viewings of the plasma in one reading. The Vista Chip II CCD detector measures all wavelengths in a single reading, providing higher precision, shorter analysis time and less argon consumption per sample. Overall, the 5110 ICP-OES delivers fast warm-up, high throughput, high sensitivity, and the largest dynamic range.

- **Reliability:** the 5110 ICP-OES features a vertical plug-and-play torch allowing measurement of the most challenging matrices. The quick and simple torch loader mechanism automatically aligns the torch and connects gases for fast startup and reproducible, consistent performance, irrespective of the operator.

- **Flexibility:** for high throughput applications, a fully integrated Advanced Valve System (AVS 6/7) six or seven port switching valve can be easily added into the 5110 ICP-OES.[1]

This application note describes the determination of micronutrients Cu, Fe, Mn, Zn, Co, Ni and heavy metals Cd and Pb in a DTPA extracted soil sample using the Agilent 5110 ICP-OES. For comparison purposes of sample analysis time and argon gas consumption, results were also obtained using the 5110 ICP-OES fitted with the integrated Advanced Valve System (AVS 6) six port switching valve.

Experimental

Instrumentation

All measurements were performed using an Agilent 5110 SVDV ICP-OES configured with an SPS 4 autosampler. The sample introduction system consisted of a SeaSpray nebulizer, double-pass cyclonic spray chamber and a 1.8 mm i.d injector torch. Instrument method parameters and analyte settings are listed in Table 1.

Table 1. Agilent 5110 SVDV ICP-OES instrument and method parameters

Parameter	Setting							
	Cu	Fe	Mn	Zn	Cd	Co	Ni	Pb
Element								
Wavelength (nm)	324.754	234.350	293.305	213.857	214.439	228.615	231.604	220.353
Nebulizer	SeaSpray							
Nebulizer flow rate	0.7 L/min							
Spray chamber	Double-pass cyclonic							
Pump speed	12 rpm							
Sample pump tubing	White-white							
Waste pump tubing	Blue-blue							
RF power	1.20 kW							
Plasma flow	12 L/min							
Aux flow	1.0 L/min							
Torch	Demountable DV 1.8 mm i.d injector							
Viewing height	8 mm							
Read time	5 s							
Number of replicates	3							
Sample uptake delay	15 s							
Rinse time	5 s							
Stabilization time	15 s							
Background correction	Fitted							

Samples

Soil samples were supplied dried and ground.

Sample preparation and calibration

DTPA extraction solution: the extraction solution comprised 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.1 M triethanolamine (TEA). 1.97 g of DTPA, 1.47 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 14.92 g TEA were dissolved separately in deionized water and then combined. The pH was adjusted to 7.3 using concentrated HCl and the volume made up to 1 L with distilled water.

Sample extraction: 10 g of soil was weighed and 20 mL of DTPA extraction solution added. After shaking for 120 minutes, the sample was filtered through with 110 mm diameter filter paper.

Multi-element calibration standards: 0.01, 0.05, 0.1, 0.5 and 1.0 $\mu\text{g}/\text{mL}$ of Cd; 0.05, 0.25, 0.5, 2.5 and 5 $\mu\text{g}/\text{mL}$ of Co and Ni; 0.1, 0.5, 1.0, 5.0 and 10.0 $\mu\text{g}/\text{mL}$ of Cu, Zn and Pb; 0.5, 2.5, 5.0, 25.0 and 50.0 $\mu\text{g}/\text{mL}$ of Mn; 1.0, 5.0, 10.0, 50.0 and 100.0 $\mu\text{g}/\text{mL}$ of Fe. All calibration blanks and standards were prepared in the DTPA extraction solution.

Spiked sample: 25 mL of the highest multi-element calibration standard was made up with 25 mL of the extracted soil sample.

Working concentration range

Linear calibrations were obtained for all elements. Calibration coefficients were greater than 0.999 (Table 2), with less than 10% calibration error for each point. Figure 1 shows a calibration curve for Mn 293.305 nm up to 50 mg/kg with a correlation coefficient greater than 0.999 and less than 3% calibration error on each calibration point (Table 3).

Table 2. Wavelength and working calibration concentration range

Element and wavelength (nm)	Concentration range (mg/kg)	Concentration coefficient
Cu 324.754	0.1-10	0.999
Fe 234.350	1-100	0.999
Mn 293.305	0.5-50	0.999
Zn 213.857	0.1-10	0.999
Cd 214.439	0.01-1	0.999
Co 228.615	0.05-5	0.999
Ni 231.604	0.05-5	0.999
Pb 220.353	0.1-10	0.999

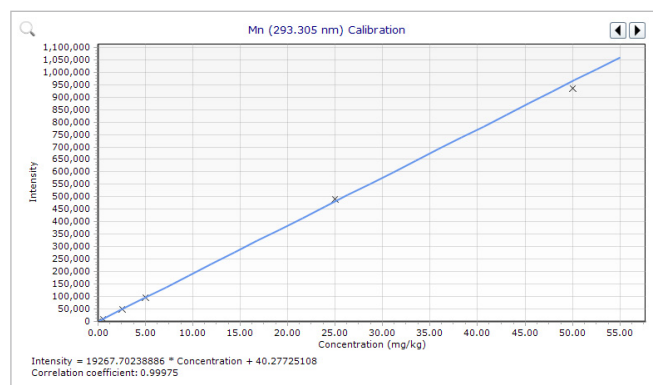


Figure 1. The calibration curve for Mn 293.305 nm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99975.

Table 3. Calibration error (%) for each calibration point for Mn 293.305 nm.

Standards	Concentration (mg/kg)	Calibration error (%)
Blank	0.0	0.00
Standard 1	0.5	1.98
Standard 2	2.5	0.92
Standard 3	5.0	0.05
Standard 4	25.0	1.88
Standard 5	50.0	2.74

Results and discussion

Method Detection Limits

The Method Detection Limits (MDLs) shown in Table 4 are based on three sigma of ten replicate measurements of the blank DTPA extraction solution, based on a sample weight of 10 g during the analytical run. The results are an average of 6 determinations, performed on two separate instruments. The MDL of each element was found to be less than 0.025 mg/kg.

Table 4. Agilent 5110 SVDV ICP-OES MDLs based on a sampling weight of 10 g for the DTPA extraction

Element	Wavelength (nm)	MDL (mg/kg)
Cu	324.754	0.003
Fe	234.350	0.012
Mn	293.305	0.005
Zn	213.857	0.002
Cd	214.439	0.002
Co	228.615	0.005
Ni	231.604	0.008
Pb	220.353	0.025

Spike recoveries

All elements were determined in the soil extract. The spike recoveries shown are the average of the results obtained from two analytical runs on two instruments i.e. n=4 of the spiked sample (Table 5). All spike recoveries were within $\pm 10\%$ of the expected values.

Table 5. Spike recoveries for all elements in the DTPA extracted soil sample obtained using an Agilent 5110 SVDV ICP-OES

Element and wavelength (nm)	DTPA extracted soil sample (mg/kg)	Spiked conc. (mg/kg)	Measured spike conc. (mg/kg)	Recovery (%)
Cu 324.754	0.93	5	4.76	95
Fe 234.350	12.62	50	46.27	93
Mn 293.305	0.76	25	23.5	94
Zn 213.857	0.12	5	4.77	96
Cd 214.439	0.002	0.5	0.47	94
Co 228.615	0.07	2.5	2.37	96
Ni 231.604	0.06	2.5	2.37	95
Pb 220.353	0.55	5	4.76	95

Advanced Valve System: Comparison of results

The Agilent Advanced Valve System (AVS 6) is a fully integrated switching valve system, designed for the Agilent 5110 ICP-OES to deliver simpler, faster, more cost effective sample analysis [1, 2]. To test this premise, the spike recovery test was repeated using the 5110 fitted with the AVS 6 (6 port valve). The valve settings shown in Table 6 were selected using the AVS Parameter Calculator in the ICP Expert software.

Table 6. Agilent Advanced Valve System settings

Parameter	Setting
Loop volume	0.5 mL
Pump rate: Valve uptake	37.5 mL/min
Pump rate: Inject	9.9 mL/min
Valve uptake delay	4.4 s
Bubble injection time	2.2 s
Preemptive rinse time	1.7 s
Stabilization time	5 s
Rinse time	0 s

Spike recoveries for all elements in the DTPA extracted soil sample obtained using the 5110 fitted with the AVS 6 are given in Table 7. The results are the average of 3 spike replicates in a single analytical run. All results are within $\pm 10\%$ of the expected values, matching the performance of the results collected without a valve system.

The AVS 6 reduces sample analysis time by almost 50% (Table 8), without compromising the accuracy of the method. This boosts sample throughput and productivity, while at the same time reducing argon consumption.

Table 7. Spike recoveries for all elements in the DTPA extracted soil sample obtained using the Agilent 5110 SVDV ICP-OES with AVS 6

Element and wavelength (nm)	Spiked concentration (mg/kg)	Measured spike concentration (mg/kg)	Recovery (%)
Cu 324.754	5	4.89	98
Fe 234.350	50	47.71	95
Mn 293.305	25	23.88	96
Zn 213.857	5	4.89	98
Cd 214.439	0.5	0.49	97
Co 228.615	2.5	2.43	97
Ni 231.604	2.5	2.41	96
Pb 220.353	5	4.86	97

Table 8. Comparison of analysis time and argon consumption per sample

	5110 without AVS 6	5110 with AVS 6
Analysis time (s)	59	30
Sample-to-sample Ar consumption (L/sample)	17.1	8.7

Conclusions

Agilent's 5110 SVDV ICP-OES with vertical torch and 27MHz SSRF system provides the robustness required for analysis of nutrients and heavy metals in DTPA extracted soil samples.

The 5110 ICP-OES combines the robust qualities of a vertically-oriented plasma with the sensitivity benefits of an axially-viewed plasma to obtain good linearity over a wide concentration range and excellent method detection limits. The method was validated with spike recoveries obtained within $\pm 10\%$ of target values, demonstrating the accuracy of the developed method.

Running the same method on a 5110 ICP-OES fitted with an Agilent AVS 6 switching valve system led to a significant reduction in sample analysis time and cut argon consumption by almost 50%.

References

1. AVS tech note, Agilent publication, 2016, 5991-6863EN
2. John Cauduro, Ultra-high speed analysis of soil extracts using an Advanced Valve System installed on an Agilent 5110 SVDV ICP-OES, Agilent publication, 2016, 5991-6853EN

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