Determination of available micronutrients in DTPA extracted soils using the Agilent 4210 MP-AES

Application note

Food safety and agriculture

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Introduction

Micronutrient soil analysis is commonly conducted in agricultural laboratories to assess the quality of soil for plant development and crop yield. Micronutrients such as copper, iron, manganese and zinc can be extracted from soil using solutions containing chelating agents such as diethylenetriaminepentaacetic acid (DTPA).

Typically, the determination of micronutrients in soils is conducted using Flame Atomic Absorption Spectroscopy (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES); however, with agriculture labs increasingly under pressure to reduce operating costs and improve safety, Microwave Plasma Atomic Emission Spectroscopy (MP-AES) is gaining recognition as a suitable alternative to these techniques.

Why use MP-AES over traditional techniques?

The advantages of MP-AES for the analysis of environmental samples, including soils include:

- Lower running costs and improved safety.
  MP-AES uses nitrogen gas from either a Dewar or extracted from air using the Agilent 4107 Nitrogen Generator. Eliminating the need for expensive and hazardous gases such as acetylene allows for unattended analysis. It is the ideal instrument for laboratories looking to reduce on-going operating costs or with safety concerns.

- Excellent analytical performance for difficult samples.
  The stable microwave plasma is capable of analyzing complex matrices such as DTPA soil extracts or soil digests containing high total dissolved solids (TDS), as well as aqueous solutions.

- Multi-elemental analysis.
  MP-AES offers improved analytical performance, lower detection limits and a wider calibration range compared to Flame Atomic Absorption Spectroscopy.

- Ease of use.
  MP-AES uses intuitive MP Expert software and plug-and-play hardware to simplify instrument setup, method development and analytical performance, with minimal training. Additionally, application specific software applets can be created in MP expert from pre-set templates, further simplifying analysis.

This application note describes the determination of micronutrients Cu, Fe, Mn and Zn in soils following DTPA extraction using the Agilent 4210 MP-AES.

Experimental

Instrumentation

All measurements were performed using the Agilent 4210 MP-AES with it's integrated humidifier accessory and SPS 4 autosampler. The instrument was set up with the standard sample introduction system comprising the Agilent OneNeb Series 2 nebulizer, double-pass glass cyclonic spray chamber and Easy-fit torch. Instrument method parameters and analyte settings are listed in Table 1.

Table 1. Agilent 4210 MP-AES instrument and method parameters.

Parameter	Value			
Element	Cu	Fe	Mn	Zn
Wavelength (nm)	324.754	259.940	257.610	213.857
Nebulizer	OneNeb Series 2			
Nebulizer flow rate (L/min)	0.75			
Pump rate (rpm)	15			
Sample pump tubing	Orange/Green Solvaflex			
Waste pump tubing	Blue/blue Solvaflex			
Read time (s)	3			
Number of replicates	3			
Sample uptake delay (s)	35			
Rinse time (s)	20			
Stabilization time (s)	10			
Background correction	Auto			
Gas source	Dewar nitrogen			

Standard and sample preparation

The soil samples were supplied dried and ground. The extraction solution comprised 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M calcium chloride dihydrate ($CaCl_2.2H_2O$) and 0.1 M triethanolamine (TEA).

1.97 g of DTPA, 1.47 g $CaCl_2.2H_2O$ and 13.3 mL TEA were dissolved separately in distilled water and combined. The pH was adjusted to 7.3 using conc. HCl and the volume made up to 1 L with distilled water.

10 g of soil was weighed and 20 mL of the DTPA extraction solution was added. After shaking for 120 minutes, the sample was filtered using filter paper.

Multi-element calibration standards were prepared at the following concentrations: 0.5, 2.5 and 5.0 µg/mL of Cu and Zn, 5.0, 25.0 and 50.0 µg/mL of Mn and 25.0, 50.0 and 100.0 µg/mL of Fe. All calibration blanks and standards were prepared in the DTPA extraction solution.

Results and discussion

Working concentration range

Linear calibrations were obtained for all four elements with calibration coefficients greater than 0.999 (Table 2) and less than 10% calibration error for each point. As an example, Figure 1 shows the calibration curve for Cu 324.754 nm and the calibration error for each calibration point (Table 3).

Table 2. Wavelength and working calibration concentration range.

Element and line (nm)	Concentration range (µg/mL)	Concentration coefficient
Cu 324.754	0.5-5	1.000
Fe 259.940	10-100	0.999
Mn 257.610	5-50	0.999
Zn 213.857	0.5-5	0.999

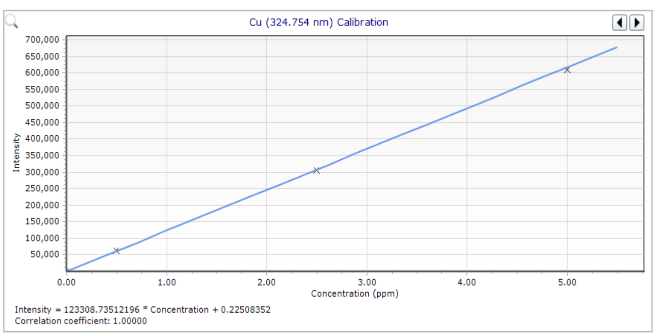

Figure 1. The calibration curve for Cu 324.754 nm shows excellent linearity across the calibrated range with a correlation coefficient of 1.00000.

Table 3. Calibration error (%) for each calibration point for Cu 324.754 nm.

Standards	Calibration error (%)
Blank	0.00
Standard 1	1.31
Standard 2	0.59
Standard 3	0.94

Method detection limits

Three sigma method detection limits (MDL) were determined from ten replicate measurements of the 0.5 µg/mL spiked blank DTPA extraction solution during the analytical run. The results shown in Table 4 are the average of 3 analytical runs.

Table 4. Agilent 4210 MP-AES element wavelengths used for analysis and MDLs at a sampling weight of 10 g for the DTPA extraction.

Element	Wavelength (nm)	MDL (mg/kg)
Cu	324.754	0.06
Fe	259.940	0.03
Mn	257.610	0.03
Zn	213.857	0.05

Spike recoveries

To verify the accuracy of the method, a DTPA-extracted soil sample was spiked with Cu, Fe, Mn and Zn at 5, 40, 20 and 5 mg/kg concentration levels respectively. The recoveries for the spiked sample are given in Table 5. The recovery results were within ± 10% of the expected value for all 4 analytes which highlights the suitability of the method for the application.

Table 5. Agilent 4210 MP-AES spike recoveries for all elements in the DTPA extracted soil sample.

Element and line (nm)	DTPA extracted soil sample (mg/kg)	Spiked concentration (mg/kg)	Measured concentration (mg/kg)	Recovery (%)
Cu 324.754	0.43	5	4.58	92
Fe 259.940	22.81	40	36.46	91
Mn 257.610	6.56	20	18.09	90
Zn 213.857	0.23	5	4.62	92

Long term stability

Long term stability of the Agilent 4210 MP-AES was measured by analyzing a DTPA extracted soil sample approximately every 2 minutes over 3 hours of continuous measurement. Figure 2 shows that excellent stability was achieved, with measurement precision <2% RSD for all elements (see Table 6), over the 3-hour period.

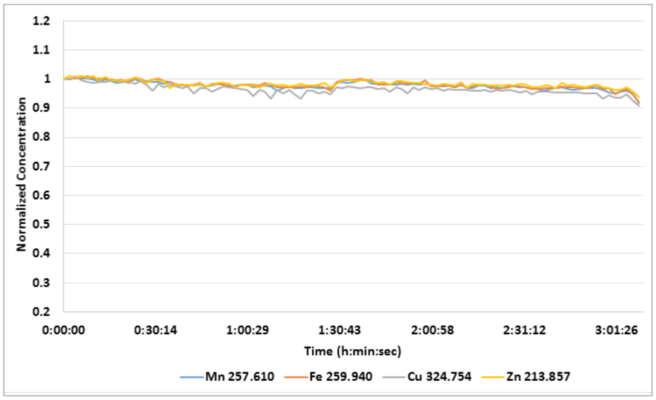

Figure 2. Normalized concentration of Cu, Fe, Mn and Zn in DTPA extracted soil sample, measured over 3 hours.

Table 6. Agilent 4210 MP-AES long term stability results (% RSD) for Cu, Fe, Mn and Zn in DTPA extracted soil sample.

Element	Wavelength (nm)	%RSD
Cu	324.754	1.77
Fe	259.940	1.45
Mn	257.610	1.38
Zn	213.857	1.21

Conclusions

The Agilent 4210 MP-AES proved suitable for the cost-effective analysis of micronutrients in DTPA extracted soil samples. As the microwave plasma is generated from nitrogen gas, it eliminates the need for expensive and flammable gases, which reduces operational costs and improves lab safety. Compared to FAAS, the high plasma temperature (5000 K) of MP-AES provides a higher sample matrix tolerance, lower detection limits and an expanded working concentration range.

The method used in this study demonstrated:

- High analytical performance with excellent MDLs and spike recoveries for all elements within ± 10% of the target values.
- Excellent linearity across a wide concentration range.
- Excellent long term stability, with less than 2% RSD over a 3-hour period.

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Published September 1 2016
Publication number: 5991-7250EN

Agilent Technologies