

## Determination of metals in soil by microwave plasma - atomic emission spectrometry (MP-AES) using DTPA extraction

### Application note

Agriculture

#### Authors

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#### Abstract

Samples of soil were analyzed for metal content using an Agilent 4100 Microwave Plasma–Atomic Emission Spectrometer (MP-AES). Extraction of the metals was performed using an extraction mixture containing diethylene-triaminepentaacetic acid (DTPA). Cd, Cr, Cu, Fe, Mn, Pb and Zn concentrations were quantitated. Both the sample introduction system and MP Expert software features were utilized to minimize interference caused by the matrix. Detection limits were between 0.4–103.0 µg/L and reproducibility was verified by comparing different analytical techniques, such as, flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma – optical emission spectrometry (ICP-OES).



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## Introduction

Determination of the concentration of metals in soil is extremely important due to the adverse effects associated with metal accumulation to toxic concentrations. Contribution to metal accumulation comes from continual treatment of the soil with fertilizers, pesticides, and other products used in agriculture. Oversupplied metals absorbed by crops, introduced through standard agricultural practices, can lead to poor crop yield and possible entry into the food chain [1]. Other sources of metal contamination for soils are discharge of effluents from industrial processes, rural domestic sewage, indiscriminate use of pesticides/fertilizers and disposal of solid waste onto inappropriate sites [2].

One the most efficient and utilized methods to evaluate the bio availability of micronutrients in soil is DTPA extraction. This principle of this extraction method consists of complexing metals with a chelating agent with careful control of the pH. The chelating agent reacts with free ions in solution creating a soluble complex resulting in the reduced activity of free metals in solution [1, 3]. This procedure has become the official method for the extraction of micronutrients (Cu, Fe, Mn and Zn) in soils in the State of São Paulo (Brazil). Note that while Cd and Pb are not considered micronutrients, they were included in this analysis due to the chelating agent reacting with the elements in solution.

Generally, determination of these elements was carried out by FAAS or ICP-OES. This application note describes a conventional analytical method for sample preparation (extraction with DTPA) for determination of micronutrients in soil using an Agilent 4100 MP-AES. The nitrogen plasma of the MP-AES provides reduction in the operational and maintenance costs of the instrument. An air compressor is required to supply a nitrogen gas generator, which feeds nitrogen to the microwave plasma. No additional gas source is used to run the instrument. The instrument produces a

stable and robust plasma using magnetically-coupled microwave energy. Combining this with an efficient sample introduction system like the inert OneNeb nebulizer produces results with precision for soil samples prepared with DTPA extraction.

## Experimental

### Instrumentation

All measurements were performed using an Agilent 4100 MP-AES. The sample introduction system consisted of PVC peristaltic pump tubing (white/white and blue/blue), a single-pass glass cyclonic spray chamber and the OneNeb nebulizer. The Agilent MP Expert software was used to automatically subtract the background signal from the analytical signal. A background spectrum from a blank solution was recorded and automatically subtracted from each standard and sample solution that was analyzed. The software was also used to optimize the nebulization pressure and the viewing position for each wavelength selected to maximize sensitivity. Because of this optimization, and considering that all determinations were carried out sequentially, each analyte was determined under optimized conditions. A standard reference solution was used to quickly and easily optimize the parameters.

Tables 1 and 2 list the instrumental operating conditions used in the determination of metals in soils using DTPA extraction.

**Table 1.** Instrument parameters for Agilent 4100 MP-AES for soil analysis using the DTPA extraction method

Instrument parameter	Operating condition
Nebulizer	Inert OneNeb
Spray chamber	Cyclonic single-pass
Read time (s)	2
Number of replicates	3
Stabilization time (s)	10
Background correction	Auto

**Table 2.** Wavelength, viewing position, nebulizer pressure and calibration fit utilized for determination of Cd, Cu, Cr, Fe, Mn, Pb and Zn by MP-AES using the DTPA extraction method

Element	Wavelength (nm)	Viewing position (mm)	Nebulizer pressure (kPa)	Calibration fit
Cd	228.802	10	100	Linear
Cr	425.433	-10	180	Linear
Cu	324.754	0	120	Linear
Fe	259.940	10	100	Linear
Mn	257.610	10	100	Linear
Pb	405.781	0	140	Linear
Zn	213.857	10	80	Rational

### Materials

Sample preparation utilized PVC flasks (10 cm<sup>3</sup>), polyethylene conical flasks, shaker with rotation of 220 rpm, filter paper, pH meter; volumetric and automatic pipettes and beakers for sample and solution preparation. Glassware was washed with detergent and soaked overnight in a solution of hydrochloric acid (HCl) 10% (v/v).

### Solutions

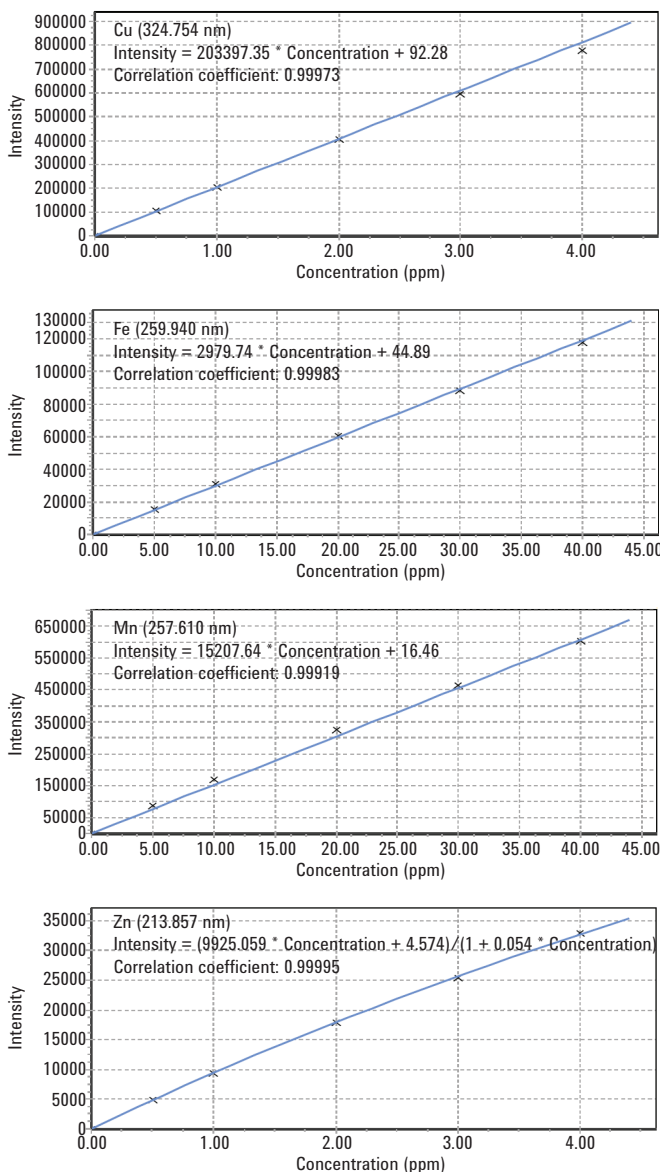
To prepare the DTPA extraction solution, 200 mL of ultra-pure water was added to 1.96 g of DTPA (Aldrich) and 14.9 mL of triethanolamine (Merck) and agitated for complete dissolution. 1.47 g of CaCl<sub>2</sub>·2H<sub>2</sub>O (Merck) was then added. The solution was made to volume in a volumetric flask (1 L) with ultra-pure water. The pH of the solution was adjusted to 7.3 with 4 mol/L HCl. The low volume of HCl used to adjust pH in 7.3 did not cause PbCl<sub>2</sub> precipitation. The 4 mol/L HCl was prepared by adding 33 mL of concentrated HCl (Merck) to 50 mL of ultra-pure water and the volume made to a total of 100 mL with ultra-pure water.

A multi-element solution containing Cd, Cu, Cr, Pb, Zn (50mg/L) and Fe and Mn (500 mg/L) (Specsol ICP-G475) was utilized to prepare elemental calibration solutions. This multi-element solution was prepared using the DTPA extraction mixture to ensure matrix matching was carried out. Concentrations of the calibration solutions were 0.5, 1.0, 2.0, 3.0 and 4.0 mg/L of Cd, Cr, Pb and Zn and 5, 10, 20, 30 and 40 mg/L of Fe and Mn. Figure 1

illustrates the calibration curves obtained for Cu, Fe, Mn and Zn for MP-AES.

### Preparation of extraction solution

In polyethylene conical flasks, 20cm<sup>3</sup> volume of soil was mixed with 40 mL of the DTPA solution. The flasks were covered and shaken by horizontal-circular movements for 2 hrs at 220 rpm. The samples were prepared in triplicate. After this step, suspensions were immediately filtered.



**Figure 1.** Calibration fit obtained for Cu, Fe, Mn and Zn by MP-AES

## Results

Limits of detection (LOD) and limits of quantification (LOQ) were calculated from three and ten times the standard deviation for 14 consecutive blank measurements. Table 3 outlines the values obtained for all elements by the 4100 MP-AES and FAAS. From this data, the results showed the capability and high detection power of the 4100 MP-AES. Detection limits obtained for Cd, Cu and Fe were 5, 14 and 29 times better than FAAS, respectively. Some elements had comparable detection limits to radial ICP-OES [4]. The plasma generated by magnetically-coupled microwave energy is especially advantageous when compared with FAAS, because it does not require a source gas (acetylene and/or nitrous oxide) and the MP-AES generated better analytical throughput. The manual analysis time for the 4100 MP-AES for this application ranged from 40–60 s for seven elements. The short time for this analysis compares with throughput of ICP-OES but the MP-AES does not require high consumption and costs of argon gas.

To evaluate the repeatability of the extraction method, all elements were determined by MP-AES, FAAS and ICP-OES. Results are presented in Tables 4–8. Concentrations of Cd and Cr in the samples are below the detection limits obtained. Due to the low level concentration of Pb in the samples, the comparative study was carried out only on the MP-AES and ICP-OES, not the FAAS. To check if there is a statistical difference between instruments, a variance analysis was undertaken and results showed that determination in different instruments had agreement to a 95% confidence level ( $\alpha = 0.05$ ). In addition, a randomized factorial design and Tukey multiple range test at the 95% level of confidence ( $\alpha = 0.05$ ) was used for testing significant differences for determination of the micronutrients Cu, Fe, Mn and Zn by DTPA method with different instruments (Table 9).

**Table 3.** Instrument parameters for Agilent 4100 MP-AES for soil analysis using DTPA extraction solution

Element	MP-AES		FAAS	
	LOD ( $\mu\text{g/L}$ )	LOQ ( $\mu\text{g/L}$ )	LOD ( $\mu\text{g/L}$ )	LOQ ( $\mu\text{g/L}$ )
Cd	3.3	10.9	17.0	56.6
Cr	0.4	1.4	*	*
Cu	2.8	9.3	40.0	133.2
Fe	8.6	28.6	250.0	832.5
Mn	3.1	10.4	5.0	16.6
Pb	103.0	343.1	*	*
Zn	30.2	100.4	15.0	49.9

\*LOD for Cr and Pb by FAAS were not calculated

## Conclusion

Determination of metals in soil employing DTPA extraction, using the 4100 MP-AES to quantitate the concentration of the metals, is a simple and effective procedure that can be easily implemented in routine samples with precision. Furthermore, because the 4100 MP-AES runs on air, it eliminates the need for acetylene, argon and nitrous oxide, which reduces operational and maintenance costs. Detection limits obtained were better than FAAS and comparable to radial ICP-OES. The results of statistical analysis indicates that the Agilent 4100 MP-AES is a technique applicable for metals determination in soil samples using the DTPA extraction method.

## References

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**Table 4.** Determination of Cu in soil samples using DTPA extraction solution by MP-AES, FAAS, and ICP-OES (n = 3)

Cu	mg/L					
	MP-AES		ICP-OES		FAAS	
	Samples	Results	R.S.D. (%)	Results	R.S.D. (%)	Results
1	0.28 ± 0.01	3.57	0.250 ± 0.005	2.00	0.32 ± 0.01	3.12
2	1.17 ± 0.02	1.70	1.23 ± 0.02	1.62	1.21 ± 0.08	6.61
3	0.98 ± 0.02	2.04	1.09 ± 0.02	1.83	1.12 ± 0.05	4.46
4	1.65 ± 0.03	1.81	1.75 ± 0.02	1.14	1.70 ± 0.05	2.94
5	2.03 ± 0.04	1.97	2.23 ± 0.04	1.79	2.29 ± 0.16	6.98
6	0.27 ± 0.01	3.70	0.29 ± 0.01	3.44	0.38 ± 0.05	13.15
7	1.12 ± 0.02	1.78	1.24 ± 0.01	0.80	1.28 ± 0.01	0.78

**Table 5.** Determination of Fe in soil samples using DTPA extraction solution by MP-AES, FAAS, and ICP-OES (n = 3)

Fe	mg/L					
	MP-AES		ICP-OES		FAAS	
	Samples	Results	R.S.D. (%)	Results	R.S.D. (%)	Results
1	5.83 ± 0.28	4.80	6.45 ± 0.09	1.39	6.42 ± 0.92	14.33
2	3.42 ± 0.02	0.58	3.93 ± 0.08	2.03	3.67 ± 0.27	7.35
3	17.44 ± 0.59	3.38	19.22 ± 0.35	1.82	18.03 ± 1.29	7.15
4	4.49 ± 0.15	3.34	4.79 ± 0.07	1.46	4.29 ± 0.17	3.96
5	2.35 ± 0.15	6.38	2.19 ± 0.07	3.19	3.25 ± 1.94	59.69
6	6.23 ± 0.28	4.49	7.10 ± 0.15	2.11	6.31 ± 1.12	17.74
7	2.85 ± 0.05	1.75	2.93 ± 0.04	1.36	2.72 ± 0.20	7.35

**Table 6.** Determination of Mn in soil samples using DTPA extraction solution by MP-AES, FAAS, and ICP-OES (n = 3)

Mn	mg/L					
	MP-AES		ICP-OES		FAAS	
	Samples	Results	R.S.D. (%)	Results	R.S.D. (%)	Results
1	50.73 ± 0.41	0.80	50.91 ± 1.06	2.08	51.67 ± 0.28	0.54
2	14.04 ± 0.36	2.56	16.11 ± 0.08	0.49	17.12 ± 1.34	7.82
3	5.90 ± 0.05	0.84	5.89 ± 0.19	3.22	6.27 ± 0.28	4.46
4	4.40 ± 0.16	3.63	4.57 ± 0.06	1.31	4.81 ± 0.27	5.61
5	0.88 ± 0.07	7.95	0.91 ± 0.01	1.09	1.00 ± 0.25	25
6	22.48 ± 0.98	4.35	25.96 ± 0.69	2.65	24.82 ± 1.54	6.20
7	8.30 ± 0.16	1.92	8.94 ± 0.14	1.56	9.07 ± 0.35	3.85

**Table 7.** Determination of Pb in soil samples using DTPA extraction solution by MP-AES and ICP-OES (n = 3)

Pb	mg/L			
	MP-AES		ICP-OES	
	Samples	Results	R.S.D. (%)	Results
1	< LD	-	< LD	-
2	0.54 ± 0.02	3.70	0.49 ± 0.005	1.02
3	0.62 ± 0.006	0.96	0.78 ± 0.04	5.12
4	0.13 ± 0.01	7.69	0.13 ± 0.02	15.38
5	0.17 ± 0.01	5.88	0.20 ± 0.006	3.0
6	0.23 ± 0.03	13	0.28 ± 0.005	1.78
7	0.37 ± 0.01	2.70	0.36 ± 0.004	1.11

**Table 8.** Determination of Zn in soil samples using DTPA extraction solution by MP-AES, FAAS, and ICP-OES (n = 3)

Zn	mg/L					
	MP AES		ICP OES		FAAS	
	Samples	Results	R.S.D. (%)	Results	R.S.D. (%)	Results
1	0.22 ± 0.008	3.63	0.21 ± 0.01	4.76	0.28 ± 0.01	3.57
2	0.70 ± 0.02	2.85	0.79 ± 0.02	2.53	0.79 ± 0.08	10.12
3	0.26 ± 0.006	2.30	0.26 ± 0.02	7.69	0.30 ± 0.04	13.33
4	0.43 ± 0.01	2.32	0.48 ± 0.01	2.08	0.63 ± 0.05	7.93
5	0.39 ± 0.02	5.12	0.42 ± 0.05	11.90	0.56 ± 0.02	3.57
6	0.64 ± 0.05	7.81	0.77 ± 0.04	5.19	0.50 ± 0.02	4.00
7	0.34 ± 0.02	5.88	0.34 ± 0.005	1.47	0.49 ± 0.02	4.08

**Table 9.** Average (error) for Cu, Fe, Mn and Zn, in mg/L, in soil samples using DTPA extraction solution determined by MP-AES, ICP-OES and FAAS ( $\alpha = 0.05$ )

Instrument	Cu	Fe	Mn	Pb	Zn
	'Average	'Average	'Average	'Average	'Average
MP-AES	2.60a (0.44)	23.81a (8.44)	18.98a (4.76)	0.67a (0.10)	0.78a (0.09)
ICP-OES	2.94a (0.44)	28.30a (8.44)	19.53a (4.76)	0.86a (0.10)	0.86a (0.09)
FAAS	2.96a (0.44)	29.42a (8.44)	20.58a (4.76)	-	0.96a (0.09)

1 – Average followed by the same letter in the column are not significantly different by the Tukey test, at the 5% level

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