

Atomic Absorption

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Analysis of Micronutrients in Soil by Using AA 800 Atomic Absorption Spectrophotometer

Introduction

Soil is used in agriculture, where it serves as the primary nutrient base for plants. Soil material is a critical component in the mining and construction industries. Soil serves as a foundation for most construction projects. Soil resources are critical to the environment, as well as to food and fiber production. Waste management often has a soil component. Land degradation is a human-induced or natural process which impairs the capacity of land to function. Soils are the critical

component in land degradation when it involves acidification, contamination etc. Soil contamination at low levels is often within soil capacity to treat and assimilate. Many waste treatment processes rely on this treatment capacity. Exceeding treatment capacity can damage soil biota and limit soil function. Derelict soils occur where industrial contamination or other development activity damages the soil to such a degree that the land cannot be used safely or productively. The analysis of soils is an excellent measure of soil fertility. It is a very inexpensive way of maintaining good plant health and

maximum crop productivity. The standard soil test provides the status of phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), pH, cation exchange capacity, lime requirement index, and base saturation. Additional tests are also available for iron (Fe), zinc (Zn), manganese (Mn), soluble salts, and nitrates. Soil fertility fluctuates throughout the growing season each year. The quantity and availability of mineral nutrients are altered by the addition of fertilizers, manure, compost, mulch, and lime or sulfur, in addition to leaching. Furthermore, large quantities of mineral nutrients are removed from soils as a result of plant growth and development, and the harvesting of crops. The analysis of soils will determine the current fertility status. It also provides the necessary information needed to maintain the optimum fertility year after year.

In the present work we compare the performance of Mehlich-I extraction with that of microwave digestion for the determination of several micronutrients in soil samples.

Experimental

The measurements were performed using the PerkinElmer® AAnalyst™ 800 atomic absorption spectrophotometer (PerkinElmer, Inc., Shelton, CT, USA) (See Figure 1) equipped with WinLab32™ for AA Version 6.5 software, which features all the tools needed to analyze samples, report and archive data and ensure regulatory compliance. PerkinElmer's high-efficiency double-beam optical system and solid-state detector provide outstanding signal-to-noise ratios and Deuterium background correction eliminates most interferences. A PerkinElmer corrosion-resistant nebulizer, which can be used for solutions containing hydrofluoric acid, was used for all flame absorption measurements. A single slot air-acetylene 10-cm burner head was used for all air-acetylene experiments.



Figure 1. PerkinElmer AAnalyst 800 atomic absorption spectrophotometer.

A PerkinElmer Multiwave™ 3000 microwave oven was used for the microwave-assisted digestion of soil samples. This is an industrial-type oven which can be equipped with various accessories to optimize the sample digestion. In this case, the samples were digested in the Rotor 8XF100 comprising eight 100 mL high pressure vessels made of PTFE-TFM in their respective protective ceramic jackets. TFM is chemically modified PTFE that has enhanced mechanical properties at high temperatures compare to conventional PTFE. This vessel has a “working” pressure of 60 bar (870 psi) and can operate at temperatures up to 260 °C. A Pressure/Temperature (P/T) Sensor Accessory was also used for this work. The P/T sensor simultaneously measures temperature and pressure for one vessel. All vessels’ temperatures were monitored with the IR Temperature Sensor Accessory. This device gives thermal (over temperature) protection to the reactions in all of the vessels by measuring the temperature remotely at the bottom surface of each vessel during the digestion process.

Standards, chemicals and certified reference material

PerkinElmer NIST® traceable calibration standards in acid for atomic spectroscopy were used as the stock standards for preparing working standards. All the working standards were prepared daily with ASTM® type I water acidified in Suprapur® nitric acid (Merck®, Germany) in polypropylene vials (Sarstedt®) on volume-by-volume dilution. Micropipettes with disposable tips (Eppendorf®, Germany) were used for pipetting solutions. Certified Reference Standard for trace metals in river sediment (Lot # 0800230) and soil solution (Lot # 0733733) from High Purity Standards were used for validating the developed method. Multi element ICP standard for trace metal ions in 5% HNO₃ from Spex Certiprep®, (New Jersey, USA) prepared at midpoint of the calibration curve was used as quality control check standard. The other acids used (Sulphuric acid and hydrochloric acid) were also of Suprapur grade. (Merck®, Germany).



Figure 2. PerkinElmer Multiwave 3000 microwave digestion system.

Sample preparation

Representative soil samples were collected from three different locations and were finely ground and then passed through a 20 mesh sieve to obtain very fine particles. 5.0 g of an air-dried, ground and sieved sample was placed in an Erlenmeyer flask and 20 mL of the extracting solution (0.05 N HCl + 0.025 N H₂SO₄) was added to it. Then it was placed in a magnetic stirrer and the mixture was stirred for 20 minutes. The resulting solution was filtered through a Whatman® No 42 filter paper into a 50 mL polypropylene vial and diluted to 50 mL with the extracting solution. The analytical reagent blanks were also prepared and these contained only the acids. The above mentioned procedure is in accordance with Mehlich-I extraction.

The microwave digestion of soil samples were done in accordance with EPA Method 3052. This method is applicable to the microwave assisted acid digestion of siliceous matrices, organic matrices and other complex matrices. This method is provided as a rapid multi-element, microwave assisted acid digestion prior to analysis protocol so that decisions can be made about the site or material. The goal of this method is total sample decomposition and, with judicious choice of acid combinations, this is achievable for most matrices. Samples of soil were weighed directly into the PTFE-TFM digestion vessel liners. Sample weights were approximately 0.1 g. To each sample, 9 mL of concentrated nitric acid and 3 mL of concentrated hydrofluoric acid were added. Some vessels contained only the acids with no sample to act as analytical reagent blanks. The vessels were sealed and placed into the Rotor 8XF100 for the microwave digestion. After the digestion process, the digestate were transferred in to 50 mL polypropylene vials and were made up to 25 mL with ASTM® type I water.

Results and discussion

The Mehlich-I extraction will give an indication about the amount of extractable micronutrients in soils. If one needs to know the total metal content, complete decomposition of samples with a microwave digestion is the preferred choice. A four point calibration with three standards and one blank was used to calibrate all the micronutrients of interest. The WinLab version 6.5 software has several quality control check options. A minimum correlation coefficient of 0.995 was assigned in the software for QC check. Quality control

check standard was prepared at the midpoint of calibration for all elements, from a multi-element ICP grade standard. The quality control check performed immediately after calibration and also at the end of analysis was ensured to fall within EPA set limits of 90-110%. The two reference materials from High Purity Standards, river sediment and the soil solution were analyzed to validate the method developed. The recoveries from both the solutions were excellent. Further post-digestion spike recovery studies were performed for one selected sample for all the nutrients under study and the results are given in the table. From Table 7 one can see the clear difference between the amounts of metal ions recovered by using the two different procedures. The Mehlich-I extraction gave lower values as expected which gave indication about the extractable metal ions and the microwave digestion gave the total metal content in the soil samples. The agreement between sample duplicates was excellent. If one needs to carry out further characterization of soil samples, procedures regarding sample collection and treatment can be modified to suit the recommendations of regulatory agencies.

Conclusions

A method was developed for the sequential determination of essential nutrients in soil by using AAnalyst 800 atomic absorption spectrophotometer. Sensitivity and accuracy in flame AA are directly correlated to the optimization of the burner position as well as the gas flows. Careful optimization of these parameters, which are different for each element, maximizes sensitivity and can significantly reduce or eliminate interferences. The unique computer-controlled, motorized burner system and gas controls allow precise, automated adjustments. Since WinLab32 software allows optimized burner position and gas flows to be stored with an element method, each element in a sequential multi-element run can be determined using its own optimized parameters. The ability of PerkinElmer/Anton-Paar Multiwave 3000 microwave digestion system to digest the soil samples in accordance with EPA Method 3052 was demonstrated. The method detection limits obtained indicates that the reliable analysis of micronutrients in difficult matrices such as soil samples is possible with the AAnalyst 800 atomic absorption spectrophotometer. The analysis of reference materials and excellent spike recovery results gave further proof to the accuracy of the developed method.

Table 1. Experimental Conditions of AAnalyst 800.

Element	Cu	Fe	Mn	K	Na	Mg	Zn
Wavelength (nm)	324.8	248.3	279.5	766.5	589	285.2	213.9
Slit (nm)	0.7	0.2	0.2	0.7	0.2	0.7	0.7
Mode	AA	AA	AA	AA	AA	AA	AA
Flame	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac
Burner Head	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm
Calibration	Linear through zero	Linear through zero	Linear through zero	Linear through zero	Linear through zero	Non linear through zero	Linear through zero
Lamp	HCL	HCL	HCL	HCL	HCL	HCL	HCL
Lamp current, mA	15	30	20	12	8	6	10
Standards (mg/L)	1.0, 2.5, 5.0	1.0, 2.5, 5.0	0.1, 0.25, 0.5	0.1, 0.25, 0.5	0.1, 0.25, 0.5	0.1, 0.25, 0.5	0.1, 0.25, 0.5
Spiked conc. (mg/L)	2.5	2.5	0.25	0.25	0.25	0.25	0.25
Read Time (seconds)	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Replicates	3	3	3	3	3	3	3
Air Flow (L/min)	17.0	17.0	17.0	17.0	17.0	17.0	17.0
Acetylene flow (L/min)	1.5	1.5	1.5	1.5	1.5	1.5	1.3

Table 2. Results of Soil CRM analysis (Lot # 0733733).

Metal	Certified Value (µg/mL)	% Recovery in Solution (in HCl and H ₂ SO ₄)	% Recovery in Solution (in HNO ₃)
Cu	0.30	103.2	104.1
Fe	200.0	95.2	96.6
Mg	70.0	98.1	98.1
Zn	1.0	105.7	100.7
Na	70.0	105.6	98.4
K	200.0	95.4	95.2
Mn	0.10	103.5	102.7

Table 4. Results of QC Recoveries.

Metal	QC 1 (%) Extraction	QC 2 (%) Extraction	QC 1 (%) MDS	QC 2 (%) MDS
Cu	107.6	100.6	101.1	99.96
Fe	107.5	106.3	100.1	101.9
Mg	108	108	100.5	101.5
Zn	104.3	104.5	103.5	100.8
Na	100.9	99.96	100.2	98.8
K	99.2	91.4	98.8	97
Mn	101	104.9	99.64	96.6

Table 3. Results of River Sediment CRM Analysis (Lot # 0800230).

Metal	Certified Value (µg/mL)	% Recovery in Solution (in HCl and H ₂ SO ₄)	% Recovery in Solution (in HNO ₃)
Cu	1.00	102.5	105.8
Fe	1200	102.8	96.4
Mg	70.0	96.9	96.1
Zn	15.0	96.0	98.8
Na	50.0	101.6	93.8
K	150.0	100.0	98.9
Mn	8.0	96.1	102.8

Table 5. Results of Spike Recoveries.

Metal	Spike Recovery (%) for Extracted Sample	Spike Recovery (%) for Digested Sample
Cu	108.5	105.1
Fe	95.8	Conc. too high for spiking
Mg	97.7	98.8
Zn	102.8	100.4
Na	106.6	106.5
K	92.1	96.9
Mn	101.8	97

Table 6. Method Detection Limits (MDLs).

Metal	MDL (mg/kg)
Cu	0.08
Fe	0.31
Mg	0.009
Zn	0.013
Na	0.02
K	0.02
Mn	0.04

Table 7. Results of Soil Analysis.

Sample (mg/Kg)	Cu		Fe		Mg		Zn		Na		K		Mn	
	Extraction	MDS	Extraction	MDS	Extraction	MDS	Extraction	MDS	Extraction	MDS	Extraction	MDS	Extraction	MDS
Soil-1	26	257	2124	116305	408	4060	1.1	167	30	1424	379	3833	370	2268
Soil-1 duplicate	27	299	2255	131302	406	3720	1.1	191	37	1722	390	3815	387	2749
Soil-2	23	257	1489	126035	392	2138	1.1	170	35	1162	329	2068	259	2439
Soil-2 duplicate	22	312	1490	135730	383	1802	1.0	198	31	1121	309	1481	249	2640
Soil-3	15	248	418	134645	418	2975	0.3	119	25	562	104	2940	71	1907
Soil-3 duplicate	14	288	374	129465	412	2593	0.3	138	24	587	95	4442	82	2210