Atomic Absorption

Author

Praveen Sarojam, Ph.D.

PerkinElmer
Global Application Center
Mumbai, India

Analysis of Organic Fertilizers for Nutrients with AAnalyst 800 Atomic Absorption Spectrophotometer

Introduction

The fertilizer industry helps to ensure that farmers have the nutrients they need to grow enough crops to meet the world's requirements for food, feed, fiber and energy. Nutrients in manufactured fertilizers are in the form that can be absorbed readily by the plants. All of these nutrients exist in nature, but the quantities are not sufficient to meet the needs of our growing, urbanized population. Soils may be naturally low in nutrients, or they may become deficient due to nutrient removal by crops over the years without replenishment – or when high-yielding varieties are grown that have higher nutrient requirements than do local varieties. All of the essential nutrients are important but in varying quantities. Macronutrients (N, P, K, Ca, Mg, etc.) are needed by plants in large quantities. The "primary nutrients" are nitrogen, phosphorus and potassium. Today, sulphur is also considered a key macronutrient. Macronutrients include both primary and secondary nutrients. Micronutrients (or "trace elements") (Fe, Mn, Zn, Cu, Ni, etc.) are required in very small amounts for correct plant growth. They need to be added in small quantities when they are not provided by the soil. Every plant nutrient, whether required in large or small amounts, has a specific role in plant growth and food production. One nutrient cannot be substituted for another. For example, potassium activates more than 60 enzymes (the chemical substances that govern life and play a vital part in carbohydrate and protein synthesis). It improves a plant's water regime and increases tolerance to drought, frost and salinity. Plants that are well supplied with potassium are less affected by disease. Magnesium is the central constituent of chlorophyll, the green pigment in leaves that functions as an acceptor of the energy supplied by the sun: 15-20% of the magnesium in a plant is found in the green

parts. Magnesium is also involved in enzyme reactions related to energy transfer. Fertilizers are needed to obtain high yields because they supply crops with the nutrients the soil lacks. By adding fertilizers, crop yields can often be doubled or even tripled. The UN Food and Agriculture Organization (FAO) Fertilizer Program undertook extensive demonstrations and trials in 40 countries over a period of 25 years. The weighted average increase resulting from the best fertilizer treatment for wheat was about 60%. Fertilizers contribute to efficient use of land and water. They ensure the most effective use of both land and water. Where rainfall is low or crops are irrigated, the yield per unit of water used may be more than doubled and the rooting depth of the crop increased through fertilizer application.

The present work demonstrates the ability of the PerkinElmer® AAnalyst™ 800 atomic absorption spectrophotometer to analyze the micronutrients in several organic fertilizers. The results obtained from using the conventional AOAC Method 965.09 using dry ashing with a muffle furnace and EPA Method 3052, the official EPA method for the microwave digestion of siliceous and organic based samples, are compared.

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 to analyze samples, report and archive data and ensure regulatory compliance. The revolutionary double-beam design of the AAnalyst 800 provides continuous, simultaneous measurement of both sample and reference beams for flame measurements. Utilizing a high-efficiency fiber optic, the sample and reference beams are simultane-ously focused on the state-of-art, solid-state detector. This translates into increased signal-integration time (without increasing analysis time) for improved precision, detection limits and reproducibility. The totally corrosion-resistant solid titanium burner head easily installs onto the spray chamber, constructed of an inert polymeric material that provides superior performance for corrosive and high solid matrices.

The systems include an eight-lamp turret mount with built-in power supplies, for the automatic alignment of both the hollow cathode lamps and electrodeless discharge lamps. 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 10cm burner head was used for all air-acetylene elements.

A Multiwave™ 3000 Microwave Oven (PerkinElmer/Anton Paar) was used for the microwave-assisted digestion. This is an industrial-type oven which is equipped with various accessories to optimize the sample digestion.

The samples were digested using the Rotor 8XF100 that consists of eight 100 mL high pressure vessels/liners made of PTFE-TFM material protected by its individual ceramic jackets. TFM is chemically modified PTFE that has enhanced mechanical properties at high temperatures compared to conventional PTFE. This vessel/liner has a "working" pressure of 60 bar (870 psi) and operational 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 in one reference vessel/liner. All vessels' temperatures were also monitored with the IR Temperature Sensor Accessory. This measures the temperature of the bottom surface of each vessel/liner, thus providing protection in case of *over-temperature* during the process of digestion.

PerkinElmer NIST®-traceable calibration standards for atomic spectroscopy were used as the stock standards for preparing working standards. All the working standards were prepared daily in ASTM® type I water acidified with 1% Suprapur® nitric acid. Working standards were prepared in polypropylene vials (Sarstedt®) on volume-by-volume dilution. Eppendorf® (Germany) micropippetes and tips were used for pippetting solutions. Certified Reference Standard for trace metals in river sediment and soil solutions from High Purity Standards (Lot # 0800230 and Lot # 0733733) was used for quality control. Multi-element ICP standard for trace metal ions in 5% HNO_3 from Spex Certiprep®, (New Jersey, USA) prepared

Figure 1. PerkinElmer AAnalyst 800 atomic absorption spectrophotometer.

Figure 2. PerkinElmer Multiwave 3000 microwave digestion system.

at midpoint of the calibration curve was used as the quality control check standard. The nitric acid and hydrofluoric acid used were also of Suprapur® grade, from Merck® in Germany.

Sample Preparation

Three organic based fertilizer samples, one of them (Sample 3) urea, were collected from the local market. Representative fertilizer samples in fine particles were prepared by grinding them in an agate mortar with its pestle, then passing them through a 20 mesh sieve.

The microwave digestion of soil samples was performed in accordance with EPA Method 3052. This method is applicable to the microwave-assisted acid digestion of siliceous matrices, and 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 for most matrices with judicious choice of acid combinations. Approximately 0.5 g of the fertilizer sample was accurately weighed directly into the PTFE-TFM digestion vessel/liners. Nine mL of concentrated nitric acid and 3 mL of concentrated hydrofluoric acid were added to this sample. Reagent blanks were also prepared using the same volumes of these two acids. The vessels were sealed and placed into the Rotor 8XF100 for the microwave digestion. After the digestion process, the digestate liquids were transferred to the 50 mL polypropylene autosampler vials and made up in 25 mL volume with the laboratory ASTM® type I water.

Muffle furnace ashing was done as follows:

Approximately 1 g of fertilizer sample was accurately weighed into a 150 mL beaker (Pyrex®, or equivalent), charred on a hot plate and ashed for 1 to 3 hours at 500 ℃ in a muffle furnace with its door open to allow free access of air. The residue cake was ground into fine particles for dissolution in 10 mL of concentrated HCl. This solution was boiled and evaporated on a hot plate almost to dryness, while not allowing it to boil dry, then re-dissolved in 20 mL

Figure 3. Samples.

2 M HCl, boiling gently if necessary. The solution was filtered through fast filter paper into 100 mL volumetric flask. The filter paper and residue were thoroughly washed with water and drained into the volumetric flask. This final solution is analyzed directly, or with dilution with 0.5 M HCl such that its absorbance was within the concentration range of the instrument. If calcium (Ca) is to be determined, the solution was added with enough lanthanum (La) stock solution to make the final dilution to contain 1% La.

Results and Discussion

The AOAC method for the determination of nutrients in fertilizers has been performed with a laboratory grade muffle furnace. This is a time consuming process for sample digestion, whereas microwave digestion is easier and reliable when compared with conventional sample preparation.

Standard calibrations were prepared for all the metal ions of interest with three standard and one blank solution. Accuracy of the developed method was tested by analyzing two certified reference materials in solutions obtained from High Purity Standards.

The recoveries were excellent which demonstrate the accuracy and reliability of the developed method.

In order to verify the calibration curve generated, a quality control standard prepared from Spex Certiprep® was aspirated at midpoint of calibration for all the metal ions. The recovery of QC sample done immediately after calibration and at the end of analysis was excellent (within the 90-110%). To demonstrate the ability of AAnalyst 800 to work in difficult matrices, spike recovery studies were carried out and were found to have excellent results (90-110%).

Method detection limits were calculated on the basis of standard deviation of seven replicates of reagent blank (student t value of 3.14 for a confidence interval of 98%).

Conclusions

A method was developed for the sequential determination of nutrients in fertilizers by using the 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 the 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 organic matrix-based fertilizer 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. The low recovery of analytes obtained with muffle furnace ashing is due to analyte loss from evaporation. In the case of microwave digestion we had better recovery, and the time required to complete the decomposition was also shorter. The whole digestion process took one hour to complete, including cooling time. As the Multiwave 3000 system offers complete digestion of organic fertilizers in accordance with EPA Method 3052, it is the preferred technique for the sample preparation for organic based fertilizer samples.

Table 1. Experimental Conditions for AAnalyst 800.

Element	Cu	Fe	Mn	Zn	Mg	Ca
Wavelength (nm)	324.8	248.3	279.5	213.9	285.2	422.7
Slit (nm)	0.7	0.2	0.2	0.7	0.7	0.7
Mode	AA	AA	AA	AA	AA	AA
Flame	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
Calibration	Linear through zero	Linear through zero	Linear through zero	Linear through zero	Linear through zero	Linear through zero
Lamp	HCL	HCL	HCL	HCL	HCL	HCL
Lamp current, mA	15	30	20	15	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	1.0, 2.5 & 5.0
Spiked concentration (mg/L)	2.5	2.5	0.25	0.25	0.25	2.5
Read Time (seconds)	3.0	3.0	3.0	3.0	3.0	3.0
Replicates	3	3	3	3	3	3
Air Flow (L/min)	17.0	17.0	17.0	17.0	17.0	17.0
Acetylene flow (L/min)	1.5	1.5	1.5	2.0	1.5	1.3

Table 2. Results of Fertilizer Analysis.

Metal	Sample 1 (Avg. of Duplicates) MDS	Sample 1 (Avg. of Duplicates) Muffle Furnace	Sample 2 (Avg. of Duplicates) MDS	Sample 2 (Avg. of Duplicates) Muffle Furnace	Sample 3 (Avg. of Duplicates) MDS	Sample 3 (Avg. of Duplicates) Muffle Furnace
Cu	49.25 ug/g	34.0 ug/g	210.49 ug/g	211.4 ug/g	1.40 ug/g	0.83 ug/g
Fe	0.534%	48.8 ug/g	2.51%	481.4 ug/g	36.8 ug/g	41.1 ug/g
Mg	0.85%	0.57%	1.51%	1.3%	98.23 ug/g	69.8 ug/g
Ca	18.7%	16.2%	5.19%	4.2%	300 ug/g	607.7 ug/g
Zn	0.014%	92.9 ug/g	0.016%	140.5 ug/g	3.54 ug/g	2.5 ug/g
Mn	0.024%	159.3 ug/g	0.048%	512 ug/g	6.57 ug/g	1.32 ug/g

Note: MDS = microwave-assisted digestion

Table 3. Results of CRM Analysis – Soil Solution A, Lot # 0733733.

Metal	Certified Value (µg/mL)	Recovery (%)
Cu	0.30 ±0.5%	101.2
Fe	200 ±0.5%	109.4
Mg	70.0 ±0.5%	95.14
Ca	350 ±0.5%	96.0
Zn	1.0 ±0.5%	102.8
Mn	0.10 ±0.5%	105.4

Table 4. Results of CRM Analysis – River Sediment A, Lot # 0800230.

Metal	Certified Value (µg/g)	Recovery (%)
Cu	1.0 ±0.5%	104.9
Fe	1200 ±0.5%	114.9
Mg	70.0 ±0.5%	101.7
Ca	300 ±0.5%	109.4
Zn	15.0 ±0.5%	99.88
Mn	8.0 ±0.5%	99.81

Table 5. Results of QC and Spike Recovery.

Metal	QC 1 (%)	QC 2 (%)	Sample 1 Spike Recovery (%)	Sample 2 Spike Recovery (%)	Sample 3 Spike Recovery (%)
Cu	106.0	106.3	109.9	110.7	113.3
Fe	109.1	109.1	112.2	108	115.6
Mg	106.0	105.7	103.1	93.1	105.8
Ca	100.8	101.8	105.2	96.0	106.8
Zn	102.3	101.4	103	99.4	102
Mn	100.2	101.7	101.1	100.9	100.0

Table 6. Method Detection Limits (MDLs).

Metal	MDL (µg/g)
Cu	0.72
Fe	1.50
Mg	0.08
Ca	1.48
Zn	1.92
Mn	0.27

Table 7. Microwave Temperature Program.

Parameter	Optimum condition
Temperature	180 ±5.0 ˚C
Ramp time	5.5 min
Hold time	9.5 min
Cool down time	20 min
Pressure	50 bar
Amount of fertilizer	0.5 g
HF	3.0 mL
HNO_3	9.0 mL

References

1. U.S. EPA Method 3052.

2. AOAC Method 965.09.

3. http://www.ces.ncsu.edu/cumberland/fertpage/inorganic.html

4. http://en.wikipedia.org/wiki/Fertilizer