APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Trace Metal Characterization of Soils Using the Optima 7300 DV ICP-OES

Introduction

Soil testing helps diagnose soil health and guides in the development of soil-specific and crop-specific remedies. It is an indispensable tool to assure national food safety, nutritional accuracy, maintenance of soil health and enhancement of soil fertility. Based on this analysis, farmers may be advised on soil fertility to make agriculture more productive and sustainable. Micronutrient analysis in soil is becoming increasingly important, as soils across the globe are found to be deficient in one or more micronutrients. Availability and proportion of micronutrients in the soil ensures higher farming productivity. Soil analysis tests primarily focus on elements such as potassium, calcium, magnesium etc. In drier areas, micronutrients such as iron, zinc, manganese, and copper are often measured, since deficiencies of these elements are more frequently associated with soils from such areas, while excessive or toxic levels of some elements like sodium may exist. Apart from micronutrient analysis, there is a concern about environmental pollution. As a result of increased industrial activities and waste disposal, soils available for cultivation and farming are nowadays becoming increasingly contaminated with toxic heavy metals. These metals include cadmium, chromium, lead etc. which are not required for the healthy growth of crops. Hence there is a need to monitor the presence of toxic heavy metals in soils available for farming.[1-3]

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Historically, atomic absorption spectrophotometers (flame and furnace) have been the instruments of choice for most soil analysis. Recently, ICP-OES has been used to provide fast and multi-element analysis of soil samples. ICP-OES is rugged and can handle a higher dissolved solid content, which is important in the analysis of soils. However, when compared with graphite furnace atomic absorption, radially viewed ICPs have had the disadvantage of lower sensitivity. This is especially important in the application of ICP-OES to the determination of trace elements in soil. The use of axially viewed ICP-OES has extended the measurable concentration range to sub-ppb levels for many elements. Axial viewing allows ultratrace measurements because it provides a longer emission path for increased sensitivity.[4] As the analysis of soils requires determination of many elements, it can be performed economically by using a simultaneous ICP-OES. However, for this type of analysis, the matrix may vary considerably and high matrix concentrations may be observed for some samples. In these cases, a matrix-tolerant sample introduction system is just as important as hardware and software safeguards in diminishing the effect of unexpected interferences. Several ICP-OES methods are available for soil determination including U.S. EPA 200.7/200.5 in the USA, DIN 38406E22 in Germany or ISO11885 on a global level.[5-8]

The present work demonstrates the development of a simple method for soil analysis by using a high-speed, segmented charge coupled detector (SCD)-based ICP-OES instrument with the ability to set the plasma viewing orientation (radial or axial) on a wavelength basis. Microwave digestion was used to greatly limit the amount of time needed for sample preparation and also to avoid the loss of volatile analytes. The microwave digestion of soil samples was performed according to U.S. EPA 3052 protocols.[9]

Experimental

The measurements were performed using the PerkinElmer® Optima™ 7300 DV ICP-OES instrument (Shelton, CT, USA) equipped with WinLab32™ for ICP Version 4.0 software for simultaneous measurement of all analyte wavelengths of interest (Figure 1). By combining an SCD detector and an echelle optical system, the Optima 7300 DV ICP-OES can measure all wavelengths simultaneously. Its wavelength flexibility allows the end users to easily add new elements as their program changes. Other benefits of Optima for soil analysis include a 40 MHz free-running solid state RF generator designed to run user-selectably from 750 to 1500 watts (in 1 watt increments). High RF power is required to generate a robust plasma which is essential for high matrix samples like soils.

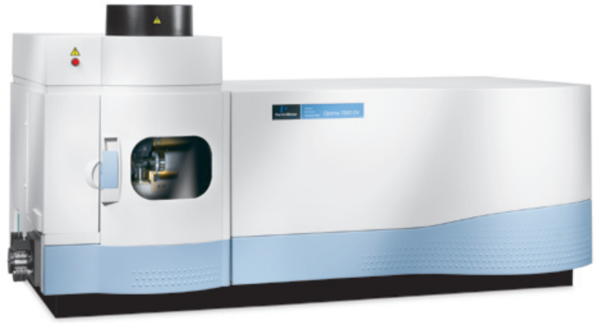

Figure 1. PerkinElmer Optima 7300 DV ICP-OES.

The ICP torch is physically mounted in a horizontal orientation in the instrument's shielded torch box and can be viewed either axially or radially. The viewing mode is user-selectable by wavelength. A shear gas provides elimination of the cool plasma tail to allow direct axial observation of the plasma's normal analytical zone, thus minimizing chemical matrix effects.

The sample introduction unit employed included a Ryton® Scott spray chamber and the GemTip™ Cross Flow Nebulizer (Figure 2). The Ryton® Scott spray chamber is made from corrosion resistant Ryton®, which is inert to most mineral acids including HF (used in this study). GemTip cross flow nebulizers are excellent general-purpose nebulizers, for the analysis of strong mineral acids, and can handle up to 5% dissolved solids (for higher dissolved solids, the GemCone™ high dissolved solids nebulizer, which can handle up to 20% dissolved solids, is recommended. This requires an end cap for use with the Ryton® Scott spray chamber). The torch position is optimized at the best position for improved performance in the presence of high dissolved solids and also to minimize injector clogging.

Figure 2. HF-resistant sample introduction unit.

The read time was set at a variable range from 1 to 5 sec using the auto-integration mode. This feature takes a snapshot of the intensities of various lines to be measured before the actual reading begins. For high intensities, a shorter time is used, while for low intensities, a longer time is used, thereby optimizing precision of analysis. Longer measurement times are beneficial in reducing shot noise, with little compromise on sample throughput (refer to Table 1 on Page 3 for detailed optimized instrumental conditions).

Table 1. **Optimized instrumental conditions for Optima 7300 DV.**

Parameter	Optimum Condition
Spray Chamber	Ryton® Scott
Nebulizer	Cross flow GemTip™
Injector	Alumina 2 mm i.d.
Sample Tubing	Standard 0.76 mm i.d. (Black-Black)
Drain Tubing	Standard 1.14 mm i.d. (Red-Red)
Quartz Torch	Single slot
Sample Capillary	Teflon® 1 mm i.d.
Sample Vials	Polypropylene
Plasma Aerosol Type	Wet
Nebulizer Start Up	Instant
RF Power	1450 Watts
Nebulizer Gas Flow	0.6 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	15 L/min
Sample Pump Rate	2 mL/min
Plasma Viewing	Axial, Radial
Processing Mode	Peak area
Auto Integration (min-max)	1-5 sec
Read Delay	60 sec
Replicates	3
Background Correction	1 or 2-point, manual

The PerkinElmer S10 Autosampler (Figure 3) was used for high throughput and automated analysis. The autosampler automates standard and sample introduction for instrument calibration and sample analysis, as well as quality control checks.

Figure 3. PerkinElmer S10 autosampler.

An Anton Paar® Multiwave™ 3000 (Austria – shown in Figure 4) was used for microwave-assisted digestion of soil samples (i.e. U.S. EPA method 3052). 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 of eight 100 mL high-pressure vessels made of PTFE-TFM in their respective protective ceramic jackets. These vessels have a working pressure of 60 bar (870 psi) and can operate at temperatures up to 260 ˚C. All vessel temperatures were monitored with the IR temperature sensor. Use of the Multiwave™ 3000 greatly reduces the amount of time required for sample preparation and the closed-vessel digestion avoids loss of volatile analytes to ensure accurate analysis.

Figure 4. Multiwave™ 3000 Microwave Digestion System.

Standards, Chemicals and Certified Reference Material

PerkinElmer NIST® traceable calibration standards in acid for ICP/AAS (N9300103, N9300141, N9300281) and SPEX CertiPrep®, standard 36-60 AS were used as the stock standards for preparing working standards. The working standards were matrix-matched with the acids used for sample digestion (refer to Table 4 on Page 4 for the combination of standards used in this study). The standards were prepared by serial volume/volume dilution in polypropylene vials (Sarstedt®, Germany). Micropipettes with disposable tips (Brand®, Germany) were used for pippetting all solutions. Certified reference standard for trace metals in river sediment (Lot No. 0800230) and soil solution (Lot No. 0733733) from High-Purity Standards (South Carolina, USA) were used for validating the developed method. Multi-element standards for ICP for trace metal ions in 5% HNO_3 from SPEX CertiPrep®, (New Jersey, USA) (Lot No. 39-86AS and Lot No. 5-139GS) were used as quality control check standards. The acids used (40% hydrofluoric, 30% hydrochloric acid and 65% nitric acid) were all of Suprapur® grade from Merck®, Germany.

Sample Preparation

Representative soil samples (one from a garden and the second one from the land of a farm house), collected from two different locations in India, were ground finely and passed through a 20 mesh sieve to obtain very fine particles. The microwave digestion of soil samples was done in accordance with U.S. EPA method 3052 (Table 2). This method is applicable to the microwave-assisted acid digestion of siliceous matrices, organic matrices and other complex matrices. The purpose of this method is total sample decomposition with a judicious choice of acid combinations suitable for most matrices. Soil samples of approximately 0.25 g each were weighed directly into the PTFE-TFM digestion vessel liners. Nine mL of concentrated nitric acid, 3.0 mL of concentrated hydrofluoric acid, 2.0 mL concentrated hydrochloric acid and 1.0 mL of hydrogen peroxide were added to each vessel. 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 microwave digestion. After digestion, the digestates were transferred to 50.0 mL polypropylene vials, and diluted to 50.0 mL with ASTM® Type I water (from a Millipore® filtration system, Millipore® Corporation, Billerica, Massachusetts, USA). Four multi-element standards were prepared such that every wavelength had at least one standard for calibration.

***Table 2.* Microwave digestion program as per U.S. EPA 3052.**

Parameter	Optimum Condition
Temperature	220±5 °C
Ramp Time	5 min 30 sec
Hold Time	9 min 30 sec
Cool Down Time	20 min
Pressure	55 Bar
Amount of Soil	0.25 g (nominal)
HF	3.0 mL
H_2O_2	1.0 mL
HCl	2.0 mL
HNO_3	9.0 mL

Results and Discussion

Wavelength selection followed U.S. EPA method 200.7 and ISO regulation 11885 and took into consideration: (a) the freedom from spectral interferences; (b) the different sensitivities against the expected concentration in the samples. The selected analytical wavelengths are compiled in Table 3. Note that in some cases, the most sensitive line was not used in order to avoid spectral interferences. The resolution of the system is sufficiently good to warrant undisturbed measurements for typical analysis of soil samples. In order to safeguard against any unexpected spectral interferences, all spectra generated during an analysis run were stored for post-analysis review. In this work, observed interferences were compensated for by modifying the processing parameters (e.g. adjusting the background correction points).

***Table 3.* List of wavelengths and calibration standards used.**

Analyte	Wavelength (nm)	Concentration of Standard (mg/L)
Al	308.212	12.0
Ba	233.520	1.0
Cd	226.499	1.0
Ca	315.881	60.0
Cr	205.557	1.0
Cu	324.756	1.0
Fe	259.934	50.0
K	766.457	10.0
Mg	279.079	30.0
Mn	257.605	1.0
Na	588.984	10.0
Ni	231.602	1.0
Pb	220.350	1.0
Sb	206.833	1.0
V	292.400	1.0
Zn	213.855	1.0

***Table 4.* Combination of calibration standards used.**

Calibration Standard	Elements
Standard 1	Cd, Cu, Cr, Mn, Ni, Pb, Sb, V, Zn
Standard 2	Ca, Fe, Na, Al, Mg
Standard 3	K
Standard 4	Ba

In order to establish the system performance, digested soil samples were measured along with standard certified reference materials. The accuracy was calculated as the difference between measured and certified concentrations (expressed in %). Please note that all the measured elements were not present in the CRMs. The results are presented in Tables 5 and 6 (Page 5). The accuracy and precision are considered very good for the analysis performed. The reproducibility of the measurement was generally below 1%. This is noteworthy because the analysis was performed in a high concentration of acid matrix, which can degrade precision.

Table 5. **Analysis of certified reference material Lot # 0733733.**

Analyte	Certified Value (mg/L)	% Recovery of Certified Value
Al	500.0	97
Ba	5.0	98
Ca	350.0	99
Cu	0.30	98
Fe	200.0	98
K	200.0	100
Mg	70.0	97
Mn	0.10	100
Na	70.0	97
Ni	0.30	96
Pb	0.40	97
V	0.10	92
Zn	1.0	99

Table 6. **Analysis of certified reference material Lot # 0800230.**

Analyte	Certified Value (mg/L)	% Recovery of Certified Value
Al	250.0	96
Ba	0.50	97
Ca	300.0	99
Cr	300.0	98
Cu	1.0	98
Fe	1200.0	98
K	150.0	100
Mg	70.0	98
Mn	8.0	98
Na	50.0	97
Ni	0.50	98
Pb	7.0	97
Sb	0.5	100
Zn	15.0	99

The validity of the calibration was monitored by the Quality Control Check section of the WinLab32 for ICP software. The quality control check standards were run at selected intervals in an unattended automatic analysis run, to ensure that the instrument performance remained consistent over the length of analysis. Table 7 provides the QC recoveries at the beginning and at the end of analysis with a time difference of ~4 hours, thereby validating consistent performance. The analysis results for the soil samples are given in Table 8. There is very good agreement between the sample results and those obtained by analysis of their duplicates.

Table 7. **Quality control check standard recoveries.**

Analyte	First QC Recovery %	Last QC Recovery %
Al	98	104
Ba	98	99
Cd	100	102
Ca	101	100
Cr	103	97
Cu	101	105
Fe	102	102
K	93	105
Mg	107	104
Mn	98	100
Na	95	97
Ni	101	100
Pb	101	99
Sb	97	96
V	104	104
Zn	100	98

Table 8. **Analysis results for soil samples.**

Analyte	Garden	Garden Duplicate	Farm House	Farm House Duplicate
Al	10.7%	10.9%	5.60%	5.50%
Ba	317 µg/g	298 µg/g	464 µg/g	418 µg/g
Cd	38.1 µg/g	36.0 µg/g	56.4 µg/g	55.0 µg/g
Ca	0.62%	0.61%	0.27%	0.25%
Cr	266 µg/g	265 µg/g	428 µg/g	431 µg/g
Cu	469 µg/g	457 µg/g	651 µg/g	658 µg/g
Fe	2.40%	2.32%	3.41%	3.47%
K	0.68%	0.69%	0.64%	0.58%
Mg	0.68%	0.70%	0.41%	0.33%
Mn	0.42%	0.41%	0.51%	0.53%
Na	0.46%	0.47%	0.44%	0.42%
Ni	204 µg/g	195 µg/g	391 µg/g	387 µg/g
Pb	35.2 µg/g	32.4 µg/g	41.6 µg/g	53.3 µg/g
Sb	74.5 µg/g	85.0 µg/g	139 µg/g	113 µg/g
V	0.09%	0.10%	0.18%	0.18%
Zn	367 µg/g	354 µg/g	390 µg/g	391 µg/g

Conclusions

The simultaneous ICP-OES (Optima 7300 DV) used in this study has the capability to analyze with good accuracy, precision, speed and robustness and fulfills the requirements normally set for the analysis of soil samples. Long-term stability (evident from QC recoveries over a period of more than 4 hours) ensures that the calibration will be consistent during the analysis run requiring fewer QC actions and possible reruns. The trace metal constitutions of soil samples were determined successfully at very low levels by using the Optima 7300 DV ICP-OES. The Multiwave™ 3000 microwave digestion system is an excellent tool for digesting soil samples as per U.S. EPA method 3052. The microwave digestion followed by ICP analysis provides the total metal content in the various soil samples analyzed. The total metal content in the soil indicates the amount of metal ions which are biologically available, available to plants, or capable of migration. This type of analysis can be used to assess soil health, identify problematic soils and their nutritional status, and aid in the development of soil-specific and crop-specific solutions. The soil collected from the farm house showed higher concentrations of toxic heavy metals such as Pb, Cd, Cr, Ni etc. when compared with the garden soil. This could be due to natural causes or may be due to the quality of water used for irrigation in the respective area. Based on this analysis, the farmers may be advised on soil-fertility management to make agriculture more productive and sustainable.

References

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