APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Accurate and Rapid Determination of 22 Major and Trace Elements in Soil with the Avio 550 Max ICP-OES

Introduction

Soil and sediments are integral parts of the earth and play a major role in food security. The elements in soil have a significant influence on the soil quality and are closely related to human and environmental health. Besides the nutritional elements (Al, Ba, Ca, Fe, K, Mg, Mn, P and Zn) that are necessary for plant growth, other trace elements in soil (Cd, Co, Cr, Pb, Mo, Ni, V, etc.) are also considered as heavy metals that can be absorbed by plants through their roots, affecting food safety and posing a potential risk to human health. Nowadays, as soil pollution has become a global concern, routine soil testing to monitor the elemental content in agricultural soils is crucially important in controlling soil pollution, maintaining ecosystem balance and protecting human health.[1] Among the analytical techniques, atomic absorption spectroscopy (AA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP mass spectrometry (ICP-MS) are commonly applied for elemental analysis in soil. Each technique has its advantages and limitations; the most suitable technique can be chosen based on the number of elements to be analyzed and their concentrations, sample throughput requirements, and the application purpose.

ICP-OES is widely used in agricultural laboratories for soil analysis due to its simultaneous multi-element measurement capability, high sensitivity, and low detection limits. This technique has been described in many standards for elemental analysis of wastes and soils, such as U.S EPA Method 200.7, EN 13346:2000 and the China standard HJ 781-2016. Additionally, U.S. EPA methods 3050B, 3051A and 3052 are the commonly used standards for sample preparation. Depending on the elements of interest and analysis purpose, a total digestion or extraction method can be used.[2-8]

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In 2016, the Chinese EPA conducted a national soil testing survey to investigate soil pollution, resulting in method HJ 781-2016, which requires the total digestion of soil samples and analysis by ICP-OES. In order to meet analytical requirements and improve efficiency, fast and accurate methodology complying with HJ 781-2016 is required for commercial laboratories. In this work, 22 major and trace elements in six certified reference soil materials were determined using the PerkinElmer's Avio® 550 Max fully simultaneous ICP-OES.

Experimental

Samples and Sample Preparation

Since soils have diverse compositions, six different soil certified reference materials (CRMs) from the China National Geophysical Research Institute were used for method development and validation: GBW07404 (GSS-4), GBW07405 (GSS-5), GBW07408 (GSS-8), GBW07428 (GSS-14), GBW07453 (GSS-24) and GBW07456 (GSS-27).

The samples were fully digested using nitric acid (HNO_3), hydrochloric acid (HCl), hydrofluoric acid (HF) and perchloric acid ($HClO_4$) following the procedure in standard HJ 781-2016. This digestion procedure can be performed using conventional hot-plate techniques, sample preparation blocks (SPB), or a microwave digestion system.

In this analysis, the SPB 50-48 digestion block from PerkinElmer was used for sample pretreatment. Compared to traditional hot plate digestion, the SPB digestion block has the advantages of being simple to use, introducing less contamination, high sample throughput, and providing a uniform temperature for reliable and reproducible operation. These advantages make the SPB well-suited for high-throughput labs.

For sample preparation, 0.25 g of each sample were weighed directly into a PTFE digestion vessel, followed by the addition of 5 mL HCl, 5 mL HNO_3, 5 mL HF and 3 mL $HClO_4$. Then, the samples were heated in SPB until white fumes from the perchloric acid appeared, and the acids evaporated almost to dryness. Then, 2 mL HNO_3 was added to dissolve the residue. When the samples were completely dissolved, the sample solution was diluted to 50 mL with deionized water. A blank solution was prepared using the same procedure without the sample.

Instrumentation

All analyses were performed with an Avio 550 Max ICP-OES using an S23 Autosampler. All hardware control, as well as data collection and interpretation, was done with Syngistix™ for ICP software. The Avio 550 Max is a fully simultaneous ICP-OES equipped with dual view, allowing major and trace elements to be measured in the same method without sample dilution. The patented Flat Plate™ plasma technology delivers a robust plasma with reduced maintenance. In addition, the vertical torch design and excellent optical resolution of the instrument enhances the ability to analyze matrix-rich samples. Plus, the S23 Autosampler offers easy-to-use automation and is fully controlled via Syngistix software.

A standard sample introduction system consisting of a MEINHARD® nebulizer and cyclonic spray chamber were used for this application. The instrumental conditions are listed in Table 1.

Table 1. Avio 550 Max ICP-OES Operating Conditions.

Parameter	Value
Nebulizer	MEINHARD® Type K
Spray Chamber	Baffled glass cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1500 W
Nebulizer Gas Flow	0.7 L/min
Auxiliary Gas Flow	0.4 L/min
Plasma Gas Flow	12 L/min
Sample Uptake Tubing	Black/Black (0.76 mm id)
Drain Tubing	Red/Red (1.14 mm id)
Replicates	3

Table 2 lists the analytes, wavelengths and view modes. Taking advantage of the Avio Max's dual view capability, radial view was used for major elements, and the axial view was used for trace elements. The chosen wavelengths are based on the sensitivity, linear dynamic range and freedom from spectral interferences. However, due to the presence of large quantities of Fe, Al and Ti in soil samples, inter-element corrections (IECs) were applied to improve the analytical accuracy and detection limits.[9]

Table 2. Elements, Wavelengths, and Plasma View Modes.

Element	Wavelength (nm)	Plasma View
Al	308.215	Radial
Ba	455.403	Radial
Be	313.107	Axial
Ca	317.933	Radial
Co	230.786	Axial
Cr	267.716	Axial
Cu	324.752	Axial
Fe	234.349	Radial
K	766.490	Radial
La	408.672	Axial
Li	670.784	Radial
Mg	285.213	Radial
Mn	257.610	Radial
Mo	202.030	Axial
Na	589.592	Radial
Ni	231.604	Axial
P	213.618	Axial
Pb	220.353	Axial
Sr	407.771	Axial
Ti	334.940	Axial
V	290.880	Axial
Zn	213.857	Axial

Preparation of Calibration Solutions

All the calibration standards were prepared with PerkinElmer multi-element standards and single-element solutions in 1% HNO_3 (v/v). Table 3 lists the concentration range of analytes in the calibration standards. To improve the accuracy, the standard solutions were prepared at concentration ranges expected in soils.

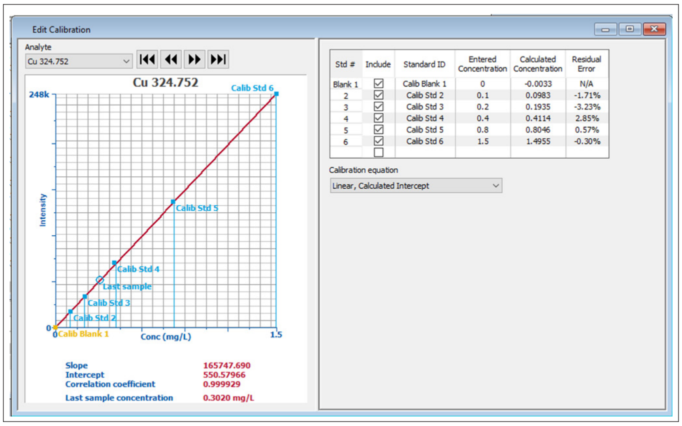
Table 3. Concentration Ranges of Calibration Standards for Major and Minor Elements.

Analytes	Concentration Ranges (mg/L)
Be, Co, Mo	0 - 0.4
Cr, Cu, Li, La, Ni , Pb, Sr, V, Zn	0 - 1.5
P, Ba, Mn	0 - 10
Ti	0 - 15
Fe, Ca, Na, Mg, K	0 - 300
Al	0 - 500

Results and Discussion

Using Smart Software to Facilitate Data Analysis

Syngistix for ICP software includes a host of smart software features to facilitate data analysis and interpretation, including smart workflow, smart methods, smart monitoring, and smart data. An example of smart data is assessing the quality of a calibration curve, which is important both when reviewing data and during method development. Figure 1 shows the Edit Calibration window which shows the calibration curve, entered standard concentrations, calculated concentrations, residual error of the calibration standards, the calibration equation, as well as the slope, intercept, correlation coefficient and concentration of the last sample analyzed. If a standard is nonconforming for any reason, it can simply be unchecked, and all information will be automatically updated instantly. During method development, it is simple to assess which type of calibration equation is most appropriate: just select a different calibration equation, and all information instantly updates.



Slope 165747.690
Intercept 550.57966
Correlation coefficient 0.999929
Last sample concentration 0.3020 mg/L

Std #	Include	Standard ID	Entered Concentration	Calculated Concentration	Residual Error
Blank 1	☑	Calib Blank 1	0	-0.0033	N/A
2	☑	Calib Std 2	0.1	0.0983	-1.71%
3	☑	Calib Std 3	0.2	0.1935	-3.23%
4	☑	Calib Std 4	0.4	0.4114	2.85%
5	☑	Calib Std 5	0.8	0.8046	0.57%
6	☑	Calib Std 6	1.5	1.4955	-0.30%
	☐				

Calibration equation: Linear, Calculated Intercept

Figure 1. Edit Calibration window in Syngistix for ICP software.

Method Detection Limits

The method detection limits (MDLs) were determined by analyzing 10 replicates of the blank solution and converting the values to mg/kg so that the MDLs are expressed in the solid sample, accounting for the dilution used in sample preparation. Figure 2 compares the MDLs of trace elements and the limits specified in China standard HJ 781-2016, showing that the MDLs are far below the required values. These data demonstrate the excellent capability of trace elemental analysis in soils. MDLs for Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, and Ti are not shown in Figure 2, since they are considered matrix elements and are present at high concentrations in soil.

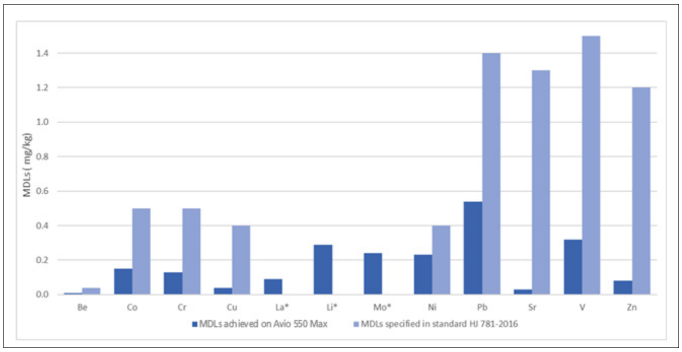


Figure 2. MDLs of trace elements achieved on the Avio 550 Max ICP-OES (dark blue) and specified in China standard HJ 781-2016 (light blue); *: MDLs are not specified in HJ 781-2016 for La, Li and Mo.

Accuracy

The accuracy of methodology was validated by analyzing five different soil CRMs. With all recoveries for all analytes in all reference materials within 10% of the certified values (as shown in Figure 3), the accuracy of the methodology is validated.

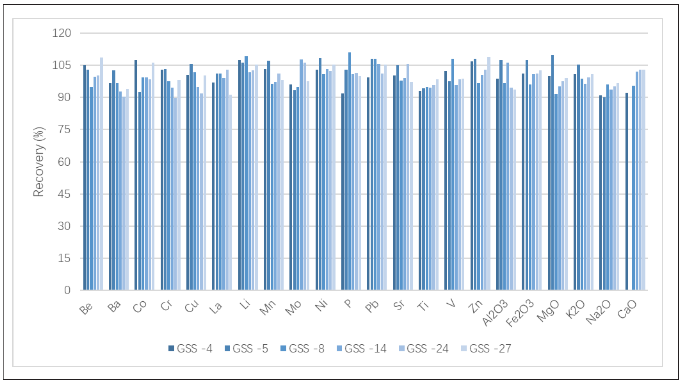


Figure 3. Analyte recoveries in soil CRMs.

Quality Control Check

In order to ensure the instrument's performance, a mid-range multi-element QC standard was run at selected intervals over two hours. As shown in Figure 4, good stability was achieved, and the recoveries of all analytes over two hours were well within ± 10%, demonstrating the robustness of the Avio 550 Max ICP-OES resulting from the Flat Plate plasma technology, PlasmaShear™, and dual view. Flat Plate plasma technology produces a robust plasma with low argon consumption. PlasmaShear is a thin stream of air which removes the top of plasma, preventing deposition on the interface window, leading to improved stability and eliminating maintenance within the interface region. The dual view capability not only allows matrix and trace elements to be measured in the same method, but radial viewing also reduces sample-induced matrix effects.

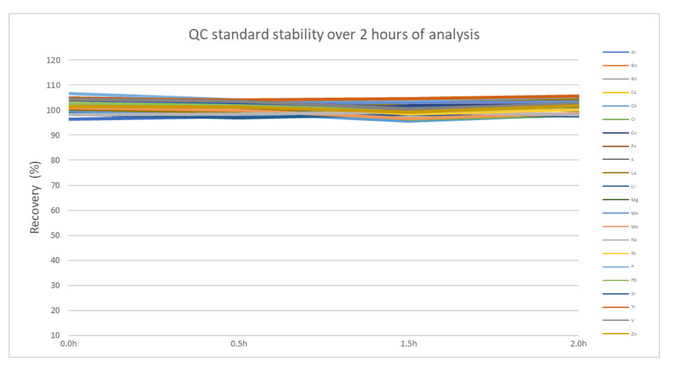


Figure 4. QC standard recoveries over a two-hour analysis.

Conclusion

In this work, a total of 22 elements in six CRM soil samples were simultaneously determined using the Avio 550 Max fully simultaneous ICP-OES. The results demonstrate the capability of Avio 550 Max to accurately measure both the major and trace elements in soil. With the use of the S23 Autosampler, the analysis is fully automated, and up to 450 samples can be measured in a single run.

The Avio 550 Max ICP-OES with Syngistix software provides simple, fast, and accurate soil analysis which fully meets the criteria of the Chinese method HJ 781-2016, providing a reliable and effective solution for the challenges faced in today's high-throughput laboratory.

References

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3. Chen Su-lan, Hu Guan-jiu, Chen Bo, Wang Xia, "Simultaneous Determination of Multi elements in Soil and Microwave Digestion and ICP-AES, Jiangsu Environmental Monitoring Center Station, 2006.
4. EPA Method 200.7 Determination of metals and trace elements in water and wastes by inductively coupled plasma atomic emission spectroscopy.
5. SW-846 EPA Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils", 1998.
6. SW-846 EPA Method 3051A, "Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils", 2007.
7. SW-846 EPA Method 3052, "Microwave Assisted Acid Digestion of Siliceous and Organically based Matrices", 1996.
8. HJ 781 Method "Solid Waste – Determination of 22 Metal Elements – ICP-OES", 2016.
9. Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, PerkinElmer, 1996.

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	N0777043
Drain Tubing	09908585
Instrument Calibration Standard 1: 5000 mg/L Ca, K, Mg, Na	N9300218 (125 mL)
Instrument Calibration Standard 2: 100 mg/L Ag, As, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl V, Zn	N9301721 (125 mL)
La Standard, 1000 mg/L	N9303780 (125 mL)
Phosphorus Standard, 1000 mg/L	N9303788 (125 mL)
Titanium Standard, 1000 mg/L	N9303806 (125 mL)
Barium Standard, 1000 mg/L	N9300181 (125 mL)
Mn Standard, 1000 mg/L	N9303783 (125 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
PTFE Digestion Tubes (6)	N9308024

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