Application News

Simultaneous ICP Atomic Emission Spectrometer   ICPE-9820

Simultaneous Multi-Element Analysis of Farmland Soil Extracts Using the ICPE-9820

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User Benefits
◆ The ICPE-9820 can quickly analyze farmland soil for multiple elements simultaneously.
◆ The ICPE-9820 can analyze high matrix samples without dilution, such as farmland soil solution extracts.

■ Introduction

Since soil contains constituents essential for crop growth that affect yield and quality, there is increasing demand for soil testing to help maintain optimum concentrations of soil constituents. Soil testing can determine the concentrations of these constituents and then create an optimized fertilization regimen to adjust them. Elemental analysis in soil testing is typically performed with an atomic absorption spectrophotometer (AAS). However, as soil testing becomes more common, there is a growing demand for faster soil analysis.

The ICPE-9820, an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) offers a wide dynamic range and can analyze multiple elements simultaneously. Soil testing analyzes soil for a large number of elements, and the ICPE-9820 can perform extremely efficient analyses that measure major and trace constituents simultaneously.

In this Application News, the ICPE-9820 analyzed farmland soil solution extracts for exchangeable constituents, available boron, trace elements and cadmium. And a spike recovery test and a dilution test were then performed to validate this analytical method.

■ Samples

The soil samples used were topsoil of high-humic cumulic andosols (TUAS-1), subsoils of high-humic cumulic andosols (TUAS-2), and sand-dune regosols (TUAS-4).

Zenkoku Tsuchi No Kai collected and extracted soil samples and provided each extract to us.

■ Sample Preparation

Each constituent tested for in soil testing requires a different extraction process with different reagents. In this Application News, three extraction reagents that are commonly used in soil testing were used to extract exchangeable constituents, available boron, trace elements and cadmium from the samples and create measurement solutions. Table 1 shows the conditions used to extract each of the target analytes.

To prevent ionization interference, strontium was added to a final concentration of 1000 mg/L in the measurement solutions used to measure exchangeable constituents.

■ Calibration Standards

Calibration standards were prepared for each test analyte to ensure matrix matching. They were prepared by mixing single-element standard solutions of B, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, and Zn. And diluting with each extraction reagent. The concentration of target elements in each calibration standard is shown in Table 2. Similar to the measurement solutions, strontium was added to a final concentration of 1000 mg/L in the calibration standards used to measure exchangeable constituents.

Table 2 Target Element Concentrations in Calibration Standards

Elements	Calibration Standards: Exchangeable Constituents (mg/L)				
	STD 0	STD1	STD 2	STD3	STD 4
Ca	0	50	100	150	200
K, Mg, Na, P, S	0	5	10	15	20
Mn	0	0.5	1	1.5	2
Ammonium Acetate	1 mol/L				
Sr	1000				

Elements	Calibration Standards: Available Boron (mg/L)				
	STD 0	STD1	STD 2	STD3	STD 4
B	0	0.5	1	1.5	2
Calcium Chloride	0.01 mol/L				

Elements	Calibration Standards: Available Trace Elements and Cadmium (mg/L)				
	STD 0	STD 1	STD 2	STD 3	STD 4
Fe	0	50	100	150	200
Mn	0	12.5	25	37.5	50
Cu, Ni, Zn	0	1.25	2.5	3.75	5
Cd, Mo	0	0.25	0.5	0.75	1
Hydrochloric Acid	0.1 mol/L				

Table 1 Extraction Conditions Used for Each Test Analyte

Test Analytes	Reagents Used for Extraction	Ratio of Reagents Added for Extraction (Soil : Reagent Ratio)	Target Element
Exchangeable Constituents	pH 7, 1 mol/L ammonium acetate solution	1:50	Ca, K, Mg, Mn, Na, P, S
Available Boron	0.01 mol/L calcium chloride solution	1:2	B
Available Trace Elements Cadmium	0.1 mol/L hydrochloric acid	1:5	Cd, Cu, Fe, Mn, Mo, Ni, Zn

◼ Equipment

The equipment used is shown in Table 3. Using a torch for high-concentration salt solution samples and a water bubbler enabled samples with a complex matrix to be analyzed without sample dilution, and the twister cyclonic spray chamber provided short analysis times and highly accurate analysis.

Table 3 Equipment

Instrument:	ICPE-9820
Nebulizer:	Nebulizer, 10UES
Chamber:	Twister cyclonic spray chamber
Torch:	Torch for High-concentration Salt Solution Samples
Autosampler:	AS-10
Other Accessories:	Water bubbler
	Peristaltic pump
	Automatic internal standard addition kit

◼ Analysis Conditions

The analysis conditions used are shown in Table 4. The plasma was viewed both axially and radially. Axial viewing allows for higher sensitivity analysis compared to radial viewing. Conversely, radial viewing only analyzes the high-temperature region of the plasma, reducing the effects of ionization interference. Soil solution extracts cause ionization interference due to their high matrix content. Since alkali earth metals are more susceptible to ionization interference, they were measured using the radial view for greater accuracy. Using both views for different purposes allows major constituents and trace constituents to be measured simultaneously without diluting the sample solutions.

In the extraction process, 0.1 mol/L hydrochloric acid was used for measuring the available trace elements and cadmium. This created a particularly high matrix content in the sample solutions, which increased the matrix effect. The analysis conditions (Table 4) used to measure the available trace elements and cadmium were selected because they are less susceptible to ionization interference. The impact of ionization interference can be reduced by increasing the plasma temperature, which is achieved by increasing the high-frequency output and reducing the sample injection volume. Also, internal standard correction can be used to correct for variability in signal intensity arising from matrix differences between calibration standards and solutions for analysis.

Table 4 Analysis Conditions

High-Frequency Output:	1.20 kW (1.40 kW)
Plasma Gas Flow:	15.0 L/min
Auxiliary Gas Flow:	1.20 L/min (1.30 L/min)
Carrier Gas Flow:	0.70 L/min (0.65 L/min)
Viewing Orientation:	Axial/Radial Viewing
Internal Standard Solution Added:	Not added (Sample: internal standard solution added in ratio of 4:1)

Conditions in parentheses were used to measure available trace elements and cadmium.

◼ Validation Testing

Calibration curves were prepared with the calibration standards (Table 2) and used to measure the amounts of exchangeable constituents, available boron, trace elements and cadmium in three farmland soil solution extracts. Table 5 shows the results of validation testing and the amounts of each targeted constituent in each solution extract. Good recoveries within 100 ± 10 % were obtained from both dilution testing and spiked recovery testing, which demonstrates the accuracy of the ICPE-9820 in analyzing farmland soil solution extracts.

Table 5 Results of Validation Testing

Test Analytes	Elements	Wavelength (nm)	Viewing Orientation	Lower Limit of Quantitation (mg/L)	TUAS-1 (mg/L)	TUAS-2 (mg/L)	TUAS-4 (mg/L)	TUAS-1 Dilution Test 10-Fold Diluted Sample (mg/L)	Dilution Test Recovery (%)	TUAS-4 Spiked Recovery Test Spiked Conc. (mg/L)	Spiked Sample (mg/L)	Spike Recovery (%)
Exchangeable Constituents	Ca	317.933	Radial	0.04	206	124	31.6	22.0	94	/	/	/
	Mg	285.213	Radial	0.01	16.9	12.1	1.80	1.84	92	10	12.0	102
	K	766.490	Axial	0.008	14.8	15.3	3.85	1.55	95	10	13.6	98
	Na	589.592	Axial	0.007	0.729	0.663	0.217			10	10.2	100
	P	213.618	Axial	0.2	0.8	0.9	3.9			10	14.0	102
	S	182.037	Axial	0.4	3.4	1.9	0.4			10	10.5	101
	Mn	257.610	Axial	0.0004	0.0568	0.103	0.182			2	2.34	108

Test Analytes	Elements	Wavelength (nm)	Viewing Orientation	Lower Limit of Quantitation (mg/L)	TUAS-1 (mg/L)	TUAS-2 (mg/L)	TUAS-4 (mg/L)	TUAS-1 Dilution Test 10-Fold Diluted Sample (mg/L)	Dilution Test Recovery (%)	TUAS-4 Spiked Recovery Test Spiked Conc. (mg/L)	Spiked Sample (mg/L)	Spike Recovery (%)
Available Boron	B	249.773	Axial	0.003	0.965	0.666	0.212	0.099	97	2	2.29	104

Test Analytes	Elements	Wavelength (nm)	Viewing Orientation	Lower Limit of Quantitation (mg/L)	TUAS-1 (mg/L)	TUAS-2 (mg/L)	TUAS-4 (mg/L)	TUAS-1 Spiked Recovery Test Spiked Conc. (mg/L)	Spiked Sample (mg/L)	Spike Recovery (%)	TUAS-2 Spiked Recovery Test Spiked Conc. (mg/L)	Spiked Sample (mg/L)	Spike Recovery (%)
Available Trace Elements & Cadmium	Cu	324.754	Axial	0.008	0.022	0.082	0.103	1	1.10	108	1	1.15	107
	Fe	259.940	Axial	0.004	0.072	0.014	5.05	1	1.09	102	1	1.06	105
	Mn	257.610	Radial	0.004	1.75	4.40	10.3	5	6.66	98	5	9.28	98
	Mo	202.030	Axial	0.01	<	<	<	1	1.05	105	1	1.04	104
	Ni	341.476	Axial	0.006	0.015	0.056	0.090	1	0.923	91	1	0.961	91
	Zn	213.856	Axial	0.004	0.452	2.33	7.49	5	5.45	100	5	7.30	99
	Cd	214.438	Axial	0.004	0.004	0.012	0.019	1	0.944	94	1	0.957	95

Lower limit of quantitation: 10 times the standard deviation of 10 repeated measurements of STD 0
<: Below the lower limit of quantitation
Dilution test recovery (%) = Sample before dilution/(10-fold diluted sample × 10) × 100
Spike recovery (%) = (Spiked sample - Unspiked sample)/Spiked concentration × 100

■ Results

Table 6 shows the values converted from the concentrations of each component in the farmland soil solution extract (Table 5) to the concentrations of the components in the soil. (All exchangeable constituents except exchangeable Mn were converted to oxides.)

Table 6 Quantitative Results (Concentration in Soil)

Test Analytes	Analyte Constituent	Lower Limit of Quantitation in Soil (mg/100 g)	Upper Limit of Calibration Curve (mg/100 g)	TUAS-1 Oxide Content in Sample (mg/100 g)	TUAS-2 Oxide Content in Sample (mg/100 g)	TUAS-4 Oxide Content in Sample (mg/100 g)
Exchangeable Constituents	CaO	0.3	1400	1441	868	221
	MgO	0.08	166	140	100	14.9
	K_2O	0.05	121	89.1	92.2	23.2
	Na_2O	0.05	135	4.91	4.47	1.46
	P_2O_5	2	229	9	10	44
	SO_4	6	300	51	29	6
	Mn	0.02 mg/kg	100 mg/kg	2.84 mg/kg	5.15 mg/kg	9.10 mg/kg

Test Analytes	Analyte Constituent	Lower Limit of Quantitation in Soil (mg/kg)	Upper Limit of Calibration Curve (mg/kg)	TUAS-1 Content in Sample (mg/kg)	TUAS-2 Content in Sample (mg/kg)	TUAS-4 Content in Sample (mg/kg)
Available Boron	B	0.006	4	1.93	1.33	0.424

Test Analytes	Analyte Constituent	Lower Limit of Quantitation in Soil (mg/kg)	Upper Limit of Calibration Curve (mg/kg)	TUAS-1 Content in Sample (mg/kg)	TUAS-2 Content in Sample (mg/kg)	TUAS-4 Content in Sample (mg/kg)
Available Trace Elements and Cadmium	Cu	0.04	25	0.11	0.41	0.52
	Fe	0.02	1000	0.36	0.07	25.3
	Mn	0.02	250	8.75	22.0	51.5
	Mo	0.05	5	<	<	<
	Ni	0.03	25	0.08	0.28	0.45
	Zn	0.02	25	2.26	11.7	37.5
	Cd	0.02	5	0.02	0.06	0.10

Lower limit of quantitation in soil (exchangeable constituents) = Lower limit of quantitation (Table 5) × Added extraction reagents as proportion of sample × 1/10 × Oxide conversion factor (exchangeable Mn not converted as oxide)

Upper limit of calibration curve in soil (exchangeable constituents) = STD 4 concentration (Table 2) × Added extraction reagents as proportion of sample × 1/10 × Oxide conversion factor (exchangeable Mn not converted as oxide)

Content in sample (exchangeable constituents) = Concentration in solution extract (Table 5) × Added extraction reagents as proportion of sample × 1/10 × Oxide conversion factor (exchangeable Mn not converted as oxide)

Lower limit of quantitation in soil (available boron and trace elements and cadmium) = Lower limit of quantitation (Table 5) × Added extraction reagents as proportion of sample

Upper limit of calibration curve in soil (available boron and trace elements and cadmium) = STD 4 concentration (Table 2) × Added extraction reagents as proportion of sample

Content in sample (available boron and trace elements and cadmium) = Concentration in solution extract (Table 5) × Added extraction reagents as proportion of sample

<: At or below lower limit of quantitation

■ Conclusion

In this Application News, the ICPE-9820 and extraction reagents normally used in soil testing were used to analyze three farmland soil solution extracts for exchangeable constituents, available boron, trace elements and cadmium. The results from validation testing show the analytical method was accurate. Using an axial view and radial view of plasma for different purposes allowed major constituents and trace constituents to be measured simultaneously without diluting samples for individual target analytes.

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