

Analysis of DTPA Extracted Soils per Chinese Standard HJ 804-2016

Simplify method development and improve confidence in results with the Agilent 5800 VDV ICP-OES and IntelliQuant Screening



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Introduction

Understanding the elemental content of soils is important for many different reasons. Nutrient elements impact plant growth and development, while an excess of heavy metals such as Cd and Pb are potentially hazardous to the ecosystem. Since soil is vital to crop and food production, many countries have programs in place to prevent soil pollution, clean up contaminated land, and improve soil quality.

In China, National Standard HJ-804 2016 describes the method for extracting bio-available elements in soil using diethylenetriaminepentaacetic acid (DTPA) for analysis using ICP-OES. The DTPA soil extraction method requires a relatively simple analytical workflow compared to other soil-preparation methods and is suitable for routine applications.

This study describes the analysis of eight bio-available elements in DTPA extracted soil using the Agilent 5800 Vertical Dual View (VDV) ICP-OES fitted with the Advanced Valve System AVS 6 and SPS 4 autosampler. The element list included: Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn.

ICP Expert smart tools

All Agilent ICP-OES are operated using Agilent ICP Expert software. ICP Expert includes smart software tools, including IntelliQuant, IntelliQuant Screening, and Early Maintenance Feedback (EMF). These tools simplify method development, minimize sample remeasurements, and increase confidence in the results.

- IntelliQuant Screening allows users to start collecting data within seconds, without having to choose which elements or wavelengths to analyze. IntelliQuant Screening helps with method development by recommending the best analyte wavelengths to use, and automatically identifying the presence of spectral interferences.
- The IntelliQuant function provides valuable insight into the sample composition, while increasing confidence in the analytical results with only a short amount of added measurement time.
- The EMF function allows the user to set up an alert to prompt maintenance after a specified number of sample-analyses rather than elapsed time. Recommended alert settings for specific sample types can be generated automatically.

Experimental

Instrumentation

The Agilent 5800 VDV ICP-OES was fitted with a SeaSpray nebulizer, double-pass glass cyclonic spray chamber, and demountable DV 1.8 mm i.d injector torch. The AVS 6 switching valve and an SPS 4 autosampler were used for the fast and automated delivery of the samples to the ICP-OES. The AVS 6, which is simple to assemble, increases sample throughput by minimizing sample uptake and rinse time. Agilent ICP Expert smart software functions including IntelliQuant, IntelliQuant Screening, and EMF were used to simplify the analysis, avoid sample remeasurements, and ensure optimum analytical performance. Instrument and AVS operating parameters are shown in Table 1 and 2 respectively.

Simplify method development with IntelliQuant Screening

Method development can be time-consuming and poorly developed methods can lead to inaccurate data being reported or remeasurements of samples. IntelliQuant Screening helps with method development. It is quick and easy to set up and there is no need to select any elements or wavelengths. IntelliQuant Screening captures data from the entire wavelength range in as little as 15 seconds, and the automatic element discovery algorithms choose the best elements and wavelengths for the analysis.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Radial	Axial
Read Time (s)	5	
Replicates	3	
Sample Uptake Delay (s)	0	
Stabilization Time (s)	0	5
Rinse Time (s)	0	
Pump Speed (rpm)	10	
Fast Pump during Uptake and Rinse (rpm)	No	
RF Power (kW)	1.3	
Aux Flow (L/min)	1.0	
Plasma Flow (L/min)	12	
Nebulizer Flow (L/min)	0.7	
Viewing Height (mm)	8	NA
Sample Pump Tubing	White-white	
Waste Pump Tubing	Blue-blue	
Background Correction	Fitted	

NA = not applicable

Table 2. AVS 6 switching valve system parameters.

Parameter	Setting
Valve Uptake Delay (s)	7
Pump Rate - Uptake (mL/min)	36.0
Pump Rate - Inject (mL/min)	9.0
Sample Loop Size (mL)	1.5
Pre-emptive Rinse Time (s)	1
Bubble Inject Time (s)	1.8

In this study, all the wavelengths chosen by IntelliQuant Screening were also suggested in the HJ-804 regulated method, indicating the reliability of the IntelliQuant algorithm. Taking Mn as an example, the HJ 804 method recommends the 257.610 and 293.305 lines, which were both given a five-star rating by IntelliQuant (Figure 1).

Figure 1 shows that five Mn lines were given a five-star rating by IntelliQuant Screening based on signal intensity, background structure, and freedom from interferences. The high confidence rating indicates that all these wavelengths are likely to be suitable for the quantitative method.

The red question mark next to the low-star rated wavelength (259.372) indicates an issue on one of the primary Mn lines. The pop-up tip shows very weak confidence in the Mn 259.372 result due to a strong Fe 259.373 interference. Based on these sample insights, Mn 259.372 was excluded from the final method.

Element	Used	Flags	Wavelength	Rating	Concentration	Intensity	Background
Mn		✓	257.610	*****	6.56	3531212.2	9240.0
			259.372	* ?	7.23	2842148.1	6717.9
			293.931	*****	6.99	767084.1	6023.2
			293.305	*****	6.93	299379.6	4272.6
			279.827	*****	6.79	108863.1	8186.8
			191.446	*****	6.43	14796.5	714.4

Analyte: Mn(259.372)
 Confidence: very weak
 Interference: Fe(259.373)
 Confidence: very strong

Figure 1. IntelliQuant star ratings for Mn wavelengths in DTPA soil extracts. Hovering over the red question mark opens the dialog box, which shows a possible Fe interference on one of the Mn prime lines.

Background correction

Fitted Background Correction (FBC) is suitable for background correction of samples with relatively clean matrices. For DTPA extracted soils, few problematic interferences are likely to arise from the matrix. The FBC technique accurately corrects background structures without user intervention. An example of automatic background fitting using FBC is shown in Figure 2. FBC provides accurate correction of background structures allowing the low-level detection of Ni 231.604.

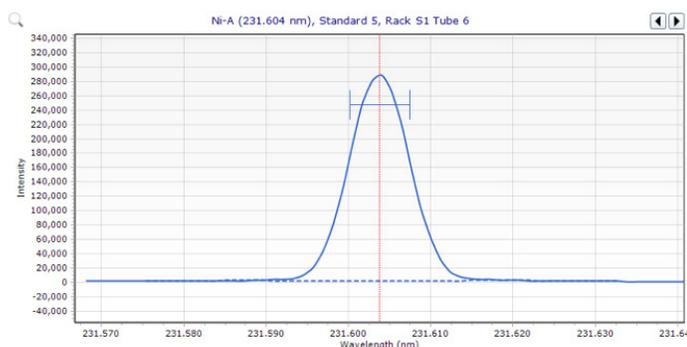


Figure 2. Automatic FBC for Ni 231.604.

Standard and sample preparation

A DTPA extraction solution was prepared in the lab following the HJ-804 method. The DTPA extraction solution comprised 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.1 M triethanolamine (TEA). 1.97 g of DTPA, 1.47 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 14.92 g TEA were dissolved separately in deionized water and then combined. The pH was adjusted to 7.3 using concentrated HCl and the volume made up to 1 L with distilled water. Calibration standards were prepared in the DTPA blank solution using Agilent single element standards. The calibration range for each element is given in Table 3.

Soil samples were prepared according to the HJ-804 regulated method. All soil samples were dried and sieved through a 2.0 mm nylon filter mesh. 10 g of sample was accurately weighed and placed in a 100 mL flask, 20 mL of DTPA extract solution was then added, 1:2 (m/v). The sample was then shaken for two hours, and then centrifuged for 10 minutes. The supernatant was filtered, providing the final extract, ready for analysis.

Calibration linearity

Linear calibrations were obtained for all analytes and wavelengths, with calibration coefficients greater than 0.99995 and Percent Relative Standard Error (%RSE) $\leq 5\%$, as shown in Table 3. A representative calibration curve for Cu 324.754 is shown in Figure 3. The calibration error for each calibration point for Cu 324.754 was $<1.2\%$, as reported in Table 4.

Table 3. Wavelength, working calibration range, and calibration information.

Element and Wavelength (nm)	Background Correction	Concentration Range (mg/L)	Viewing Mode	Correlation Coefficient	%RSE
Cd 214.439	Fitted	0.01–5	Axial	0.99997	3.3
Co 230.786	Fitted	0.01–5	Axial	0.99999	1.4
Cu 324.754	Fitted	0.01–10	Axial	1.00000	0.99
Fe 259.940	Fitted	0.1–100	Radial	1.00000	1.1
Mn 257.610	Fitted	0.01–25	Radial	1.00000	2.6
Ni 231.604	Fitted	0.05–10	Axial	0.99998	1.7
Pb 220.353	Fitted	0.1–10	Axial	1.00000	3.5
Zn 206.200	Fitted	0.1–100	Radial	0.99999	1.9

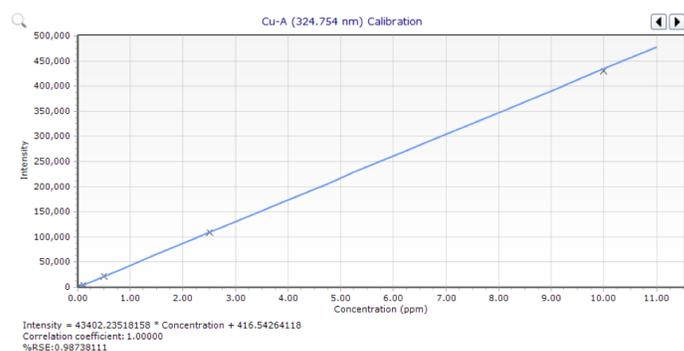


Figure 3. Calibration curve for Cu 324.754 nm shows perfect linearity across the calibrated range, with a correlation coefficient of 1.00000 and %RSE of 0.99.

Table 4. Calibration error (%) for each calibration point for Cu 324.754.

Standards	Concentration (ppm)	Calibration Error (%)
Blank	0	0.00
Standard 1	0.01	1.16
Standard 2	0.1	0.68
Standard 3	0.5	0.29
Standard 4	2.5	0.02
Standard 5	10	1.02

Results and discussion

Method detection limits

The method detection limits (MDLs) were based on three sigma of 10 repeated measurements of the blank DTPA extraction solution, taken during an analytical run. The results are an average of six runs performed on two separate instruments, based on a sample weight of 10 g.

A low-level spike recovery test was done using the blank DTPA solution. The spike levels and recoveries shown in Table 5. The recoveries are averages of six analytical measurements taken on two separate instruments.

Table 5. Method detection limits (in sample) and results of a low-level spike recovery test of the blank DTPA solution, n=6.

Element and Wavelength (nm)	MDL ($\mu\text{g}/\text{kg}$)	Spike Level (ppb)	Recovery (%)
Cd 214.439	0.28	5	103
Co 230.786	0.85	5	100
Cu 324.754	0.87	5	107
Fe 259.940	3.32	50	97
Mn 257.610	0.48	5	102
Ni 231.604	1.44	5	105
Pb 220.353	4.17	5	106
Zn 206.200	2.29	50	93

Spiked soil recoveries

The eight elements were measured in an extracted soil sample, as shown in Table 6. The soil extract was then spiked at various concentrations depending on the element, as detailed in Table 6. The spike recoveries are based on six analytical runs of the spiked soil sample on two instruments over different days. All spike recoveries are shown to be within $\pm 10\%$, demonstrating the capability using the 5800 VDV ICP-OES to analyze multiple elements accurately.

Table 6. Measured concentrations and recoveries of a spiked soil extract, n=6.

Element and Wavelength (nm)	Unspiked Sample (mg/L)	Spiked Level (mg/L)	Recovery (%)
Cd 214.439	0.156	0.5	93
Co 230.786	0.068	0.5	94
Cu 324.754	3.46	5	95
Fe 259.940	30.02	50	97
Mn 257.610	9.03	10	97
Ni 231.604	0.564	1	92
Pb 220.353	4.61	5	91
Zn 206.200	44.93	40	94

Long-term stability

A long-term stability test was carried out by analyzing 210 samples and 22 QC solutions over six hours. The average sample-to-sample analysis time was 76 s. All QC recoveries were within $\pm 10\%$ of the expected values, with RSD < 3.5% for all elements (Figure 4 and Table 7). The results demonstrate the robustness and precision of the method over six hours, without the need to recalibrate or clean the sample introduction system, minimizing instrument down-time.

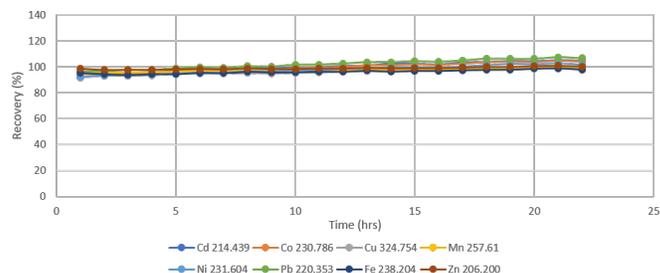


Figure 4. Recovery of a QC sample in a DTPA matrix analyzed every 10 samples over six hours.

Table 7. Percentage RSD of QC sample analyzed over six hours.

Element and wavelength (nm)	%RSD
Cd 214.439	3.3
Co 230.786	3.3
Cu 324.754	2.4
Fe 259.940	1.4
Mn 257.610	1.3
Ni 231.604	3.2
Pb 220.353	3.4
Zn 206.200	1.0

Quantitative and semiquantitative analysis

To check that the wavelengths recommended in the HJ 804 method were free of spectral interferences, IntelliQuant was used to confirm the best wavelengths. All wavelengths used for the quantitative method are recommended by the HJ 804 and were also recommended by IntelliQuant, see Figure 1.

Running IntelliQuant during the quantitative analysis can be valuable because IntelliQuant can identify and calculate semiquantitative results for 70 elements to provide a complete elemental snapshot of the sample in a matter of a seconds. Complex samples like soils often contain elements that are not in the method, so IntelliQuant can be used to identify unexpected elements.

Figure 5 shows the results of the IntelliQuant analysis. The software generates a periodic table heat map with estimated concentrations of the all elements present in the soil sample. The color-coding used to represent the concentration range for the elements is user-adjustable.

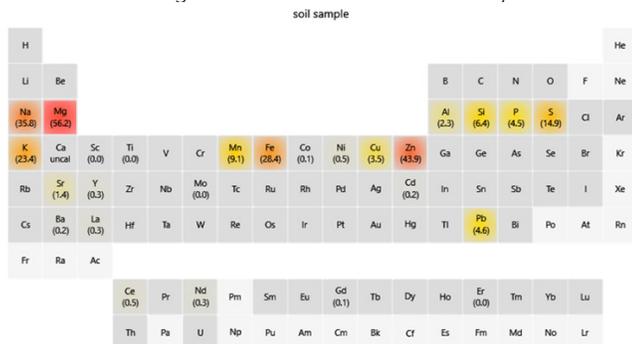


Figure 5. The IntelliQuant heat map shows relative concentrations of all elements in a sample.

For extra confidence in final results, IntelliQuant data can be used to verify the full quantitative results. As shown in Table 8, the semi-quantitative concentrations determined by IntelliQuant were within $\pm 25\%$ of the full quantitative values, providing extra confidence in the analytical results.

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Table 8. Comparison of quantitative and IntelliQuant data.

Element	Concentration (mg/L)		Element	Concentration (mg/L)	
	Quantitative	IntelliQuant		Quantitative	IntelliQuant
Cd	0.15	0.17	Mn	8.72	9.12
Co	0.07	0.05	Ni	0.54	0.54
Cu	3.30	3.46	Pb	4.38	4.63
Fe	29.3	28.4	Zn	43.9	43.9

Conclusion

The Agilent 5800 VDV ICP-OES with AVS 6 switching valve is suitable for the high throughput analysis of eight bio-available elements in DTPA soil extracts according to Chinese National Standard HJ-804.

The IntelliQuant function was used to simplify method development, assist with result validation, reduce the need for sample reruns, and increase confidence in the analytical results. Other smart tools, including Early Maintenance Feedback, help maintain instrument performance and avoid any downtime during the analysis of complex samples such as soils. Fitted background correction easily corrected the soil-matrix background structures.

The MDLs met the requirements of the regulated method and the spike recovery test showed good accuracy for the measurement of all eight bio-available elements in soils. The 5800 also demonstrated excellent stability over the six-hour QC recovery test, maximizing productivity.

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