APPLICATION NOTE

Atomic Absorption

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Simple and Reliable Determination of Heavy Metals in Soil with the PinAAcle 900H AA Spectrometer

Introduction

Soil, as the root of the food chain, plays a central role in food safety. However, according to the world soil resource report (FAO, 2015), approximately 33% of all global soil has been degraded by excessive or inappropriate development and utilization by human activities.[1] The heavy metal contamination of soil is one of the most widespread and severe environmental problems. This pollution not only decreases crop production, but also affects the health of people consuming the resulting food.[1-4] With the increased knowledge about the impact of heavy metals from food on human health, the quality of soil resources has attracted considerable attention and concern.

Because they do not degrade and are toxic, heavy metals accumulate in the human body, leading to various serious diseases, including cancer. Cadmium (Cd), lead (Pb) and chromium (Cr) are commonly regarded as extremely toxic elements since they are harmful to humans, even at low concentrations. Zinc (Zn), nickel (Ni) and copper (Cu) are essential metals for plants at trace concentrations but are toxic if present at higher concentrations. Therefore, routine monitoring of these six metals in soil is vitally important to protect the quality and safety of food.

With rapid economic expansion, the problem of soil pollution in China has become increasingly serious. To prevent and control soil pollution, the Chinese government implemented the "Ten Action Plan" and conducted a nationwide assessment of soil quality, involving the sampling and analysis of soil samples across China, which began in 2016 and is ongoing. Meanwhile, in August 2018, the Ministry of Environmental Protection of China issued new national soil quality standard GB 15618-2018 which defined the maximum concentration levels of heavy metals both in agriculture and in construction soils. Consequently, the government's environmental agencies will monitor soil quality more strictly. The risk-screening concentrations for toxic metals in agricultural and construction soils are shown in Table 1. Atomic absorption spectroscopy (AAS) is defined in standards GB 15618-2018 and GB 36600-2018 as the analytical method for the determination of these heavy metals, which are also specified as graphite furnace AA (GFAAS) for Pb and Cd analysis and flame AA (FAAS) for Cr, Cu, Ni and Zn.

As a comparison, the upper limit for these metals in other countries are listed in Table 2.

However, for analytical testing laboratories, the determination of heavy metal elements in soils has been a challenge because of the large variety of soil samples and stringent requirements for accuracy and throughput. The official Chinese standard includes a sample preparation procedure which is time-consuming and not suitable for large numbers of samples.

The conventional digestion methods for soil samples use a hot plate or microwave digestion system with with the following acid combinations: HNO_3-HCl or HNO_3-HF (EPA 3050b, EPA 3051a, EPA 3052) or HNO_3-HCl-HF-$HClO_4$ (GB 15618).[11-14] Decomposition of soil with these methods normally takes 2-3 hours and requires a large volume of acid. The more acid used, the higher the possibility of contamination and the shorter the lifetime of graphite tubes. This work discusses the development of a fast, reliable soil digestion method for the rapid and accurate determination of Cd, Cr, Cu, Ni, Pb, and Zn by atomic absorption spectroscopy.

Table 1. Regulatory limits for soils with soil pH 5.5-6.5, according to China regulations.[5,6]

Element	Risk Screening Concentrations (mg/kg)		Analytical Method	Regulated MDL* (mg/kg)
	Agriculture Soil	Construction Soil		
Pb	90	400	GFAAS	0.1
Cd	0.3	20	GFAAS	0.01
Cr Total	150	–	FAAS	5
Cr VI	–	3.0	FAAS	
Cu	50	2000	FAAS	1
Ni	70	150	FAAS	5
Zn	200	-	FAAS	0.5

* Regulated MDLs were specified in China National Standard (GB 17139, GB 17138, GB 17141, HJ 491-2009) and based on sample preparation as follows: 0.5 grams sample diluted to 50 mL

Table 2. Limiting values of heavy metals in soil (mg/kg), according to German, Dutch, Australian and Canadian regulations.[7,8,9,10]

Element	Limiting Reference Values (mg/kg)			
	Germany	Netherlands	Australia	Canada
Pb	100	85	300	45
Cd	1	0.8	3	1
Cr Total	100	100	400	67
Cu	60	36	100	62
Ni	50	35	60	37
Zn	150	140	200	290

Experimental

Standards, Chemicals and Certified Reference Materials

PerkinElmer single element standards were used as the stock standards for preparing calibration standards. All the standards were prepared with 18.2 MΩ-cm deionized water and acidified to 1% with Suprapur® nitric acid in polypropylene vials with volume-by-volume dilution.

Micropipettes (Eppendorf®, Germany) with disposable tips were used for pipetting solutions. High-purity HNO_3, HCl and HF (Suprapur®, Merck®, Germany) were used for sample acidification. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was used as matrix modifier for graphite furnace analysis.

Sample Preparation

Four different soil certified reference materials (CRMs) from the China National Geophysical Research Institute (GSS 2, GSS 8, GSS 13, GSS 14) were used for method validation. A SPB 50-48 Sample Preparation Block (SPB) system (PerkinElmer Inc., Shelton, Connecticut, USA) was used for sample pretreatment. This digestion method is based on EPA method 3052 and the China National Standard to extract the elements from the soil samples and is not intended for full decomposition of the sample.

Approximately 0.5 g of soil samples were weighed directly into 50 mL polypropylene (PP) reaction vessels. Using the same acids combination as the standard for soil samples digestion, 3.0 mL HCl, 1.0 mL HNO_3 and 2.0 mL HF (all concentrated) were added to each sample. Analytical reagent blanks were also prepared and contained only the acids. The vessels were lightly covered with the lids and placed into the block. The samples were digested at 120 °C for 1h. Following the digestion, the cooled digested sample solutions were diluted to final volume of 50.0 mL with the 18.2 MΩ-cm deionized water and then centrifuged. The supernatant solution was ready for analysis.

This digestion method provides the advantage of reducing sample preparation time and extending graphite tube lifetime by using smaller quantities of less aggressive acids. As shown in Table 3, only a total 6 mL of acid is used in this digestion procedure, compared to 10-20 mL required in other digestion methods. In addition, using the disposable PP vessels with the SPB digestion system also minimizes contamination.

Atomic Absorption Instrumentation

All measurements were performed using a PerkinElmer PinAAcle™ 900H flame/furnace AA spectrometer (PerkinElmer Inc., Shelton, Connecticut USA) equipped with Syngistix™ for AA software, version 4.0. In addition, the PinAAcle 900H could also be operated with Syngistix for AA Express software, which provides a simplified workflow and only three steps to acquire results. Both software packages feature all the tools needed to analyze the samples as well as report and archive the data. The use of cutting-edge fiber optics in PerkinElmer's PinAAcle 900 series spectrometers maximizes light throughput and improves detection limits. The high efficiency double-beam optical system and solid-state detector provide outstanding signal-to-noise ratios, and the Deuterium background correction eliminates most interferences.

The standard high-sensitivity, corrosion-resistant nebulizer assembly with Pt/Ir capillary and a single slot air-acetylene 10 cm burner head were used for all flame absorption measurements.

All graphite furnace analyses were performed with Massmann-type/HGA graphite tubes and used the AS 900 autosampler with 148-position tray. Lumina™ hollow cathode lamps (HCLs) were used for all elements.

Instrumental Operating Conditions

The instrumental parameters used with the PinAAcle 900H are shown in Tables 4 and 5 for flame and graphite furnace analyses, respectively. The graphite furnace temperature programs are listed in Table 6.

For determination of chromium by flame, as shown in Table 4, a fuel-rich (yellow) air-acetylene flame was used. The optimization of the burner position, as well as the gas flows, were optimized for best sensitivity. Another important procedure is adding 1% ammonium chloride (NH_4Cl) to all samples and standard solutions to eliminate the interference caused by iron.

Chinese standard GB 15618-2018 lists 232.0 nm as the recommended wavelength for Ni, and all results reported are with this wavelength. However, Ni 352.4 nm was also monitored and found to be more robust, due to fewer interferences from non-atomic absorbance.[15]

Table 3. Comparison of different digestion methods.

Digestion Method	Reference	Acid Volume*	Time (h)	Vessel
Microwave-Assisted Digestion	EPA 3051A; EPA 3052	~10 mL	2	PTFE digestion vessel, PP volumetric tube
Hot Plate Digestion	EPA 3050B; GB 15618	~20 mL	2 or more	PTFE beaker, PP volumetric tube
SPB Digestion	**Advanced method**	**6 mL**	**1**	**PP volumetric tubes**

* Acid volume based on the digestion of 0.2-0.5 g sample

Table 4. Instrument Operating Conditions for the Flame Analysis.

Element	Cu	Ni	Zn	Cr
Wavelength (nm)	324.75	232.0 Alternative: 352.4	213.86	357.87
Slit Width (nm)	0.7	0.2	0.7	0.7
Mode	AA	AA	AA	AA
Lamp Type	HCL*	HCL	HCL	HCL
Lamp Current (mA)	15	25	15	25
Burner Head	10 cm	10 cm	10 cm	10 cm
Calibration Standards (mg/L)	0.1, 0.2, 0.6, 0.8	0.1, 0.2, 0.4, 0.8	0.05, 0.1, 0.2, 0.3	0.2, 0.4, 0.6, 0.8
Read Time (sec)	3	3	3	3
Flame	Air-AC**	Air-AC	Air-AC	Air-AC
Acetylene Flow (L/min)	2.5	2.5	2.5	4
Air Flow (L/min)	10	10	10	10

* HCL = hollow cathode lamp

** Air-AC = air acetylene

For Pb and Cd analysis by GFAAS, according to the test standard GB 17141, a matrix modifier of 1% ammonium dihydrogen phosphate was added automatically to each standard, sample and blank with the autosampler to reduce the interference and improve the precision and accuracy of results. Alternatively, palladium nitrite could also be applied as a modifier for this application and has equivalent performance.

Results and Discussion

The goal of this work was to develop an efficient method for routine soil analysis. Using the digestion block offers the benefits of less contamination and dramatically reduced sample preparation time compared to hot plate digestion, resulting in increased sample throughput.

For both FAAS and GFAAS measurements, the calibrations were done with the method of standard addition. Excellent correlation coefficients of better than 0.999 were obtained, as shown in Figures 1 and 2.

Table 5. Instrument Operating Conditions for the Graphite Furnace Analysis.

	Pb	Cd
Wavelength (nm)	283.31	228.80
Slit Width (nm)	0.7	0.7
Mode	AA-BG*	AA-BG
Signal Measurement	Area	Area
Read Time (sec)	4	5
Lamp Type	HCL**	HCL
Lamp Current (mA)	10	5
Matrix Modifier	$NH_4H_2PO_4$	$NH_4H_2PO_4$
Sample Volume (µL)	16	16
Matrix Modifier Volume (µL)	5	5
Calibration Standards (µg/L)	12.5, 25.0, 37.5, 50.0	0.5, 1.0, 1.5, 2.0

* AA-BG = atomic absorption with background correction

** HCL = hollow cathode lamp

Table 6. Graphite Furnace Temperature Programs.

	Temp. (°C)	Ramp (s)	Hold (s)	Internal Gas Flow (mL/min)	Gas Type
Pb 283.3 nm					
Dry Step 1	120	5	20	250	Argon
Dry Step 2	150	15	20	250	Argon
Pyrolysis	700	10	10	250	Argon
Atomization	1900	0	4	0	–
Clean Out	2450	1	5	250	Argon
Cd 228.80 nm					
Dry Step 1	120	5	20	250	Argon
Dry Step 2	150	15	20	250	Argon
Pyrolysis	500	10	10	250	Argon
Atomization	1300	0	5	0	–
Clean Out	2450	1	5	250	Argon

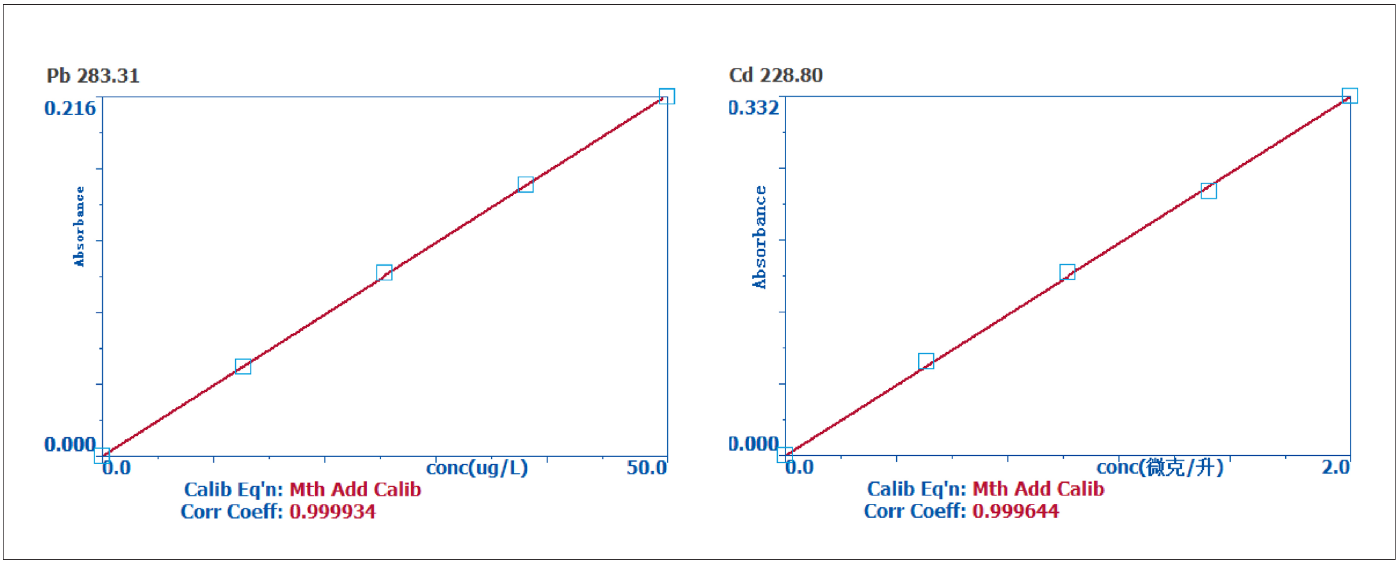

Figure 1. Calibration graphs for Pb and Cd with GFAAS.

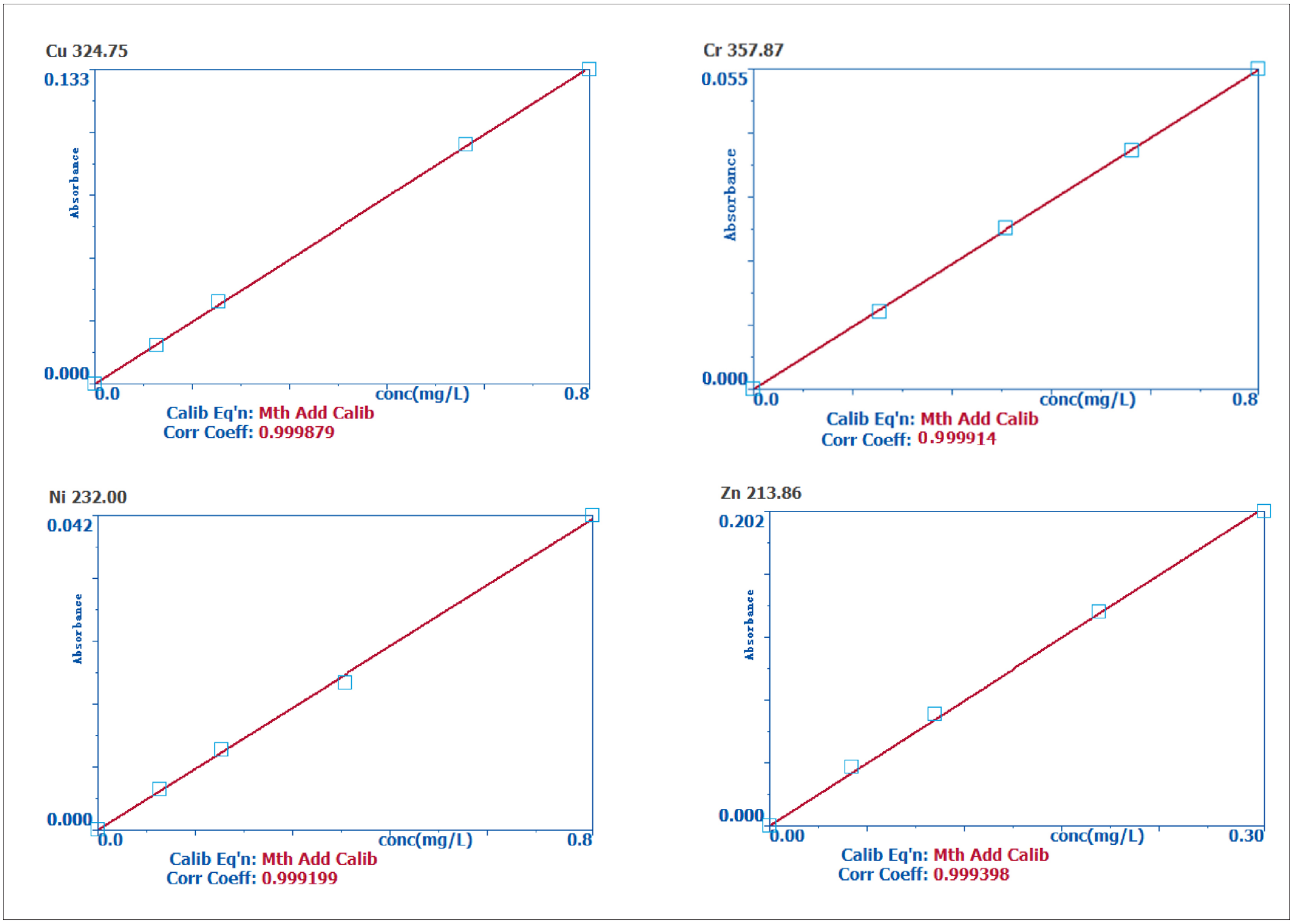

Figure 2. Calibration graphs for Cu, Cr, Ni, and Zn with FAAS.

Limits of Detection

The method detection limits (MDLs) in the solid were determined as three times the standard deviation of eleven replicates of the reagent blank and calculated with the dilution factor used in sample preparation. As shown in Figure 3, all MDLs fully meet the required MDLs specified in the China National Standard and are far below the limits listed in Tables 1 and 2.

Accuracy

The accuracy of the developed method was determined by analyzing four representative soil reference materials GSS 2, GSS 8, GSS 13, and GSS 14. The measured and certified results are compared in Tables 7 and 8, with all values falling within the certified ranges. Figure 4 graphically summarizes these results.

For analysis by GFAAS, because higher concentrations of Pb are present in the certified reference material samples, dilution was automatically performed in-line with the AS 900 autosampler so that the concentration of Pb would fall within the calibration concentration ranges for producing accurate results. The ability to auto-dilute samples with the AS 900 minimizes additional user error and saves time.

The peaks for the calibration standards are shown in Figure 5. The same appearance time and peak shape between the standards and samples demonstrate that matrix effects were effectively eliminated by using the standard addition method.

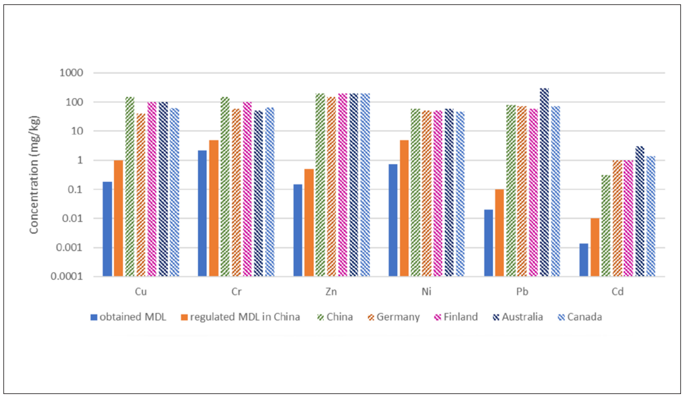

Figure 3. Experimental MDLs compared to regulated levels in the China standard and the maximum allowable concentrations in China, Germany, Netherlands, Australia, and Canada.

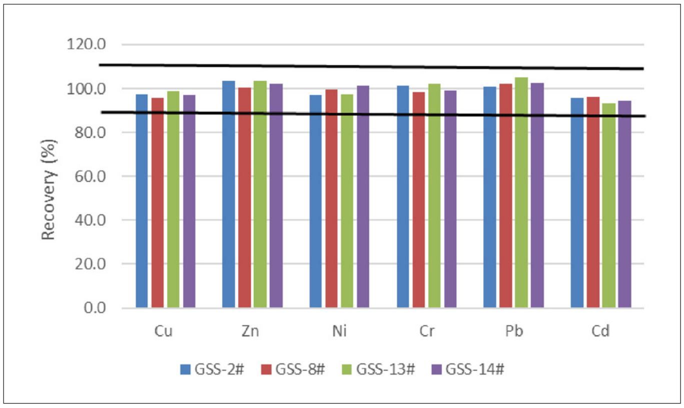

Figure 4. Recoveries of four soil certified materials.

Table 7. Results of Cu, Zn, Ni and Cr in CRM soils of GSS 2, GSS 8, GSS 13, GSS 14 with FAAS.

Soil CRM Sample		Cu	Zn	Ni	Cr
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
GSS-2#	Certified Conc.	16.3 ± 0.9	42 ± 3	19.4 ± 1.3	47 ± 4
	Measured Conc.	15.9	43.4	18.8	47.6
GSS-8#	Certified Conc.	24.3 ± 1.2	68 ± 4	31.5 ± 1.8	68 ± 6
	Measured Conc.	23.3	68	31.4	66.9
GSS-13#	Certified Conc.	21.6 ± 0.8	65 ± 3	28.5 ± 1.2	65 ± 2
	Measured Conc.	21.4	67	27.7	66.3
GSS-14#	Certified Conc.	27.4± 1.1	96 ± 3	33 ± 2	70 ± 3
	Measured Conc.	26.6	98.0	33	69

Table 8. Results of Pb and Cd in CRM soils of GSS 2, GSS 8, GSS 13, GSS 14 with GFAAS.

Soil CRM Sample		Pb	Cd
		(mg/kg)	(mg/kg)
GSS-2#	Certified Conc.	20 ± 3	0.071 ± 0.014
	Measured Conc.	20.2	0.068
GSS-8#	Certified Conc.	21 ± 2	0.13 ± 0.02
	Measured Conc.	21.5	0.13
GSS-13#	Certified Conc.	21.6± 1.2	0.130 ± 0.01
	Measured Conc.	22.7	0.121
GSS-14#	Certified Conc.	31 ± 1	0.20 ± 0.02
	Measured Conc.	31.9	0.19

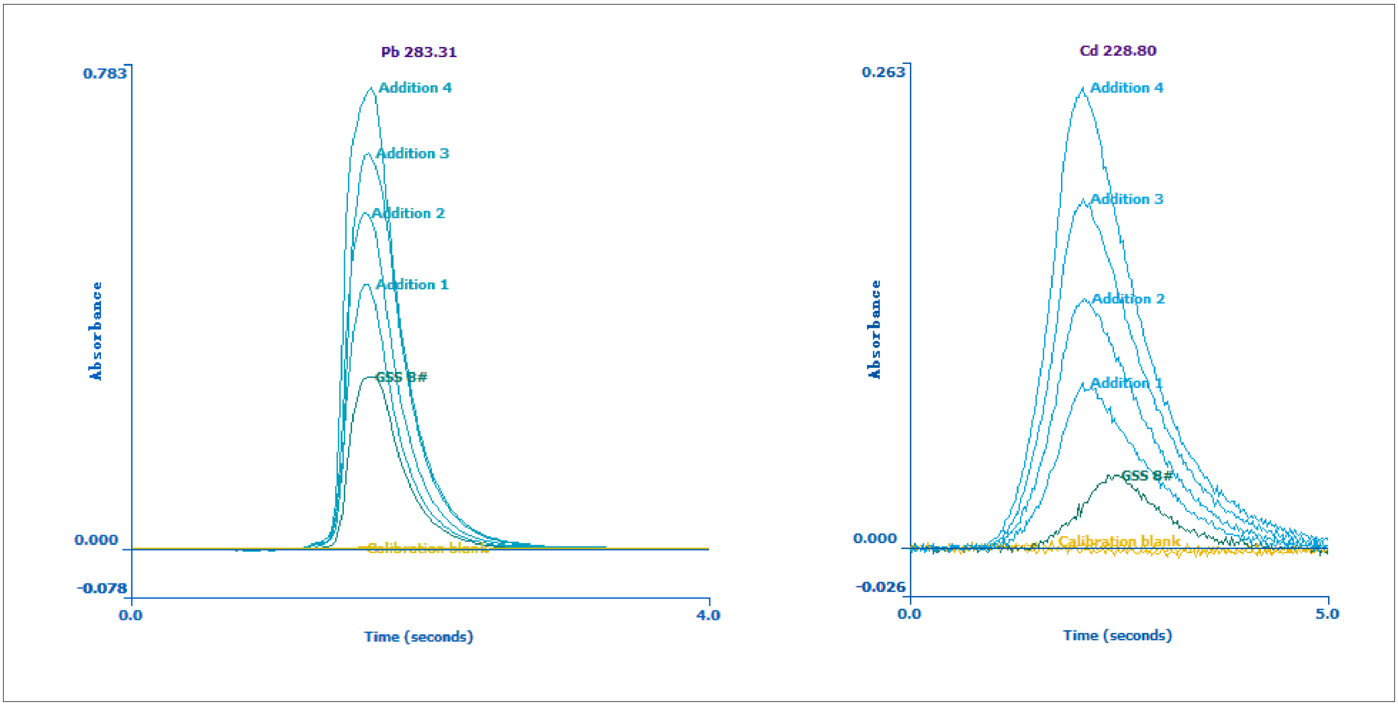

Figure 5. Overlay of spectral profiles of Pb (left) and Cd (right) in standard solutions spiked in GSS 8 sample.

Conclusion

The PinAAcle 900H AA spectrometer, equipped with both a flame and HGA graphite furnace, provides outstanding performance for analyzing a variety of soil samples over a wide range of concentrations. The combination of flame and graphite furnace in the PinAAcle 900H offers a low-cost system with the superior sensitivity required for heavy-metal testing in soil matrices. Using the SPB preparation block for the upfront sample digestion minimizes the possibility of contamination while increasing productivity for the laboratory. Equivalent results can also be obtained on the PinAAcle 900T flame/Zeeman furnace model.

The use of the AS 900 autosampler facilitates the unattended operation of the instrument. Even when a sample is beyond the calibration range, the autosampler can dilute the samples appropriately into the calibration range. Results from QC samples, standards, or any sample can be plotted using Syngistix software's QC Charting Wizard. Limit ranges, means, or expected values can be included on the chart. Quality control charts can be quickly and easily prepared.

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Accessories and Consumables Used

Component	Description	Part Number
Sample Preparation Block	SPB 50-24, 24-Position 50 mL 115/230 V SPB 50-48, 48-Position 50 mL 115/230 V	N9300802 N9300803
Conical Centrifuge Tube	50 mL, Qty 500	B0193234
Pb Lamp	Lumina Hollow Cathode Lamp	N3050157
Cd Lamp	Lumina Hollow Cathode Lamp	N3050115
Cr Lamp	Lumina Hollow Cathode Lamp	N3050119
Cu Lamp	Lumina Hollow Cathode Lamp	N3050121
Ni Lamp	Lumina Hollow Cathode Lamp	N3050152
Zn Lamp	Lumina Hollow Cathode Lamp	N3050191
HGA Graphite Tubes	Pyrocoated Graphite Tubes with Integrated Platform	B3001262 (5-pack) B3001264 (20-pack) N9300651 (40-pack)
Cd Standard	1000 ppm, Matrix 2% HNO_3	N9300176 (125 mL) N9300107 (500 mL)
Pb Standard	1000 ppm, Matrix 2% HNO_3	N9300175 (125 mL) N9300128 (500 mL)
Cu Standard	1000 ppm, Matrix 2% HNO_3	N9300183 (125 mL) N9300114 (500 mL
Cr Standard	1000 ppm, Matrix 2% HNO_3	N9300176 (125 mL) N9300107 (500 mL)
Ni Standard	1000 ppm, Matrix 2% HNO_3	N9300177 (125 mL) N9300136 (500 mL)
Zn Standard	1000 ppm, Matrix 2% HNO_3	N9300178 (125 mL) N9300168 (500 mL)
Modifier $NH_4H_2PO_4$	10% $NH_4H_2PO_4$, 100 mL	N9303445
Modifier $Pd(NO_3)_2$	1% Pd, 50 mL	B0190635
Modifier $Mg(NO_3)_2$	1% Mg, 100 mL	B0190634

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