Application Note

Environmental

China Soil Pollution Survey: Elemental Analysis of Soil and Sediment Digests by ICP-MS

Fast, accurate quantitative analysis of 16 elements using an Agilent 7800 ICP-MS with HMI

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Introduction

Pollution of soil and sediments from man-made sources is an increasing public health concern, especially in newly industrialized countries. Sources of contamination include widespread use of agricultural fertilizers and pesticides, inadequate clean-up and disposal of industrial waste, and pollution by heavy metals from mining and smelting. Leaching from urban waste sites, and emissions of airborne particulates from industry and vehicles also contribute to the level of environmental pollution. To protect the quality and safety of drinking water sources, food crops, and the wider environment, some developing countries are implementing comprehensive environmental management strategies.

As part of its commitment to improve soil quality, especially soil intended to be used to grow crops, China has developed an Action Plan for the Prevention and Control of Soil Pollution. The plan was part of China's 13th Five-Year Plan (2016–2020), which was adopted in May 2016. In 2017, a Technical Stipulation of Soil Analysis for

China Soil Pollution Survey (*1*) was established, and China also began a National Soil Pollution Survey. Nationwide in China, about 1.35 million km^2 of land (an area about twice the size of Texas, or five times bigger than New Zealand) are used for agricultural production. All this agricultural land is included in the Soil Pollution Survey, together with the lakes and rivers next to the farmland. A previous study in 2013 estimated that about 33,300 km^2 (3.33 million hectares, about the size of Belgium) were considered too contaminated to grow crops. The aim of the survey, which is due to be completed by the end of 2018, is to identify which areas of farmland are polluted and to what extent. The results will be used to guide follow-up remediation work.

The 2017 Technical Stipulation soil survey method requires the determination of eight elements, Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb in soils. As and Hg must be determined by Atomic Fluorescence Spectroscopy (AFS) following an extraction procedure. Following complete acid digestion of the soil, the other elements (or subsets of them) may be determined by ICP-MS, ICP-OES, Graphite Furnace AAS (GFAAS), or Flame AAS. Further elements, Be, V, Mn, Co, Mo, and Sn may be specified by local authorities, if their analysis is justified based on specific local pollution sources. In addition, Sb may be added to the AFS analytes, if specified locally. It is evident that the method requires multiple elements to be determined at low concentrations in very large numbers of varied soil and sediment digests. Given these method requirements, the fast, sensitive, multi-element capabilities of ICP-MS make it an ideal analytical technique (in combination with AFS) for measuring the soil and sediment samples required for the survey.

To ensure that the workflow is suitable for high throughput environmental labs, the sample preparation stage also needs to be efficient. Acid digestion of soils and sediments by open-vessel, hotplate digestion, or closed-vessel, microwave digestion is well established. But hot block digestion is very time-consuming and is prone to contamination and loss of volatiles, while conventional high-pressure microwave digestion is expensive and best-suited to small batches. By optimizing the sample digestion process, a low-pressure microwave digestion approach developed by Agilent can be used for the complete digestion of batches of 30 soil and sediment samples.

High matrix samples such as soil and sediment digests are considered challenging to analyze routinely by ICP-MS. High dissolved solids levels can cause sample matrix material to accumulate on the ICP-MS interface leading to long-term drift. Diluting the samples reduces the matrix loading, but the dilution step increases the risk of contamination and compromises detection limits. The Agilent 7800 ICP-MS is designed to handle high matrix samples containing up to 3% total dissolved solids (TDS), around 10 times higher than is typical for ICP-MS. The 7800 instrument has the robustness to handle large batches of variable, high matrix samples. The instrument also provides effective interference removal and the wide dynamic range required for accurate analysis of major and trace analytes in a single run:

1. The High Matrix Introduction (HMI) system uses a proprietary aerosol dilution approach to control the level of sample matrix delivered to the plasma. Diluting the sample in the aerosol phase, rather than the liquid phase, reduces matrix loading on the interface, while also simplifying sample preparation. HMI also reduces the signal suppression typically caused by variable sample matrices, simplifying the calibration strategy and ensuring good stability over extended runs.

2. Agilent's fourth generation Octopole Reaction System (ORS^4) is optimized for helium collision mode (He mode), giving effective control of polyatomic interferences. Helium mode uses kinetic energy discrimination (KED) to reduce the transmission of all common matrix-based polyatomic interferences under a single set of cell conditions. He mode method setup and operation are simpler and more consistent than with reactive cell gases, where cell conditions must be optimized for each different sample matrix.

3. The 7800 ICP-MS uses an Orthogonal Detector System (ODS) with 10 orders dynamic range. The ODS enables the direct analysis of major elements (100s or 1000s of ppm) and trace level analytes (single or sub-ppt) in the same run, without requiring any custom settings. The high upper concentration limit reduces sample reruns caused by over-range results, simplifying methodology and allowing labs to maintain high productivity when analyzing variable sample matrices.

This study describes the high throughput analysis of soil and sediment digests using the Agilent 7800 ICP-MS with Agilent SPS 4 autosampler, following preparation by low-pressure microwave digestion.

Experimental

Reagents

The calibration standards were prepared from a mixed multi-element ICP-MS standard (SPEX CertiPrep, NJ, USA) containing 10 ppm each of all required elements except Mo and Sb. These two elements were added from single-element stocks (1000 ppm, Kanto Chemical Co., Japan). In addition, single element stocks for the elements Mn, Cu, Zn, Ba, and Pb were added to the multi-element stock to give higher calibration levels for these major elements in the mixed standards. Initial and Continuing Calibration Verification Quality Control (QC) Standards (ICV/CCV) were prepared from Agilent Stock Standard (part number 5183-4682).

Five stream sediment certified reference materials (CRMs): GBW07307a; GBW07309; GBW07311; GBW07360; and GBW07366 (NCS, China) were digested and analyzed. The CRMs were measured unspiked and again after the addition of mixed multi-element spikes containing all elements of interest. All reagents used (HNO_3, HCl, H_2O_2, HF, and H_3BO_3) were bought from Kanto Chemical Co., Japan.

The internal standard (ISTD) solution was prepared from Agilent's Internal Standard Mix (part number 5183-4681). It contains 3 ppm ^{6}Li, Ge, In, and Bi. Rh, Lu, and Re were added from 1000 ppm single element stocks (Kanto Chemical Co., Japan).

Sample preparation using microwave digestion

The five sediment CRM samples were digested using a Mars 6 Microwave Digestion System (CEM Corporation, Japan) according to the method outlined in Figure 1.

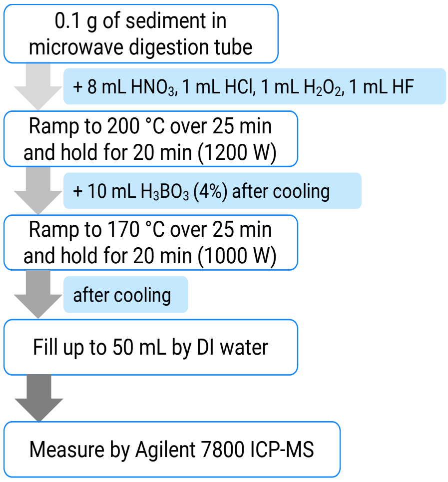

Figure 1. Microwave digestion method used for sediment sample preparation.

First, approximately 0.1 g of each CRM was digested in 8 mL HNO_3, 1 mL HCl, 1 mL H_2O_2, and 1 mL HF. The H_2O_2 was added slowly to prevent excessive bubbling within the tubes. The temperature was ramped to 200 °C over 25 min, and held for 20 min.

Once the digests had cooled, 10 mL H_3BO_3 was added to the tubes to neutralize any remaining HF before the digestion procedure was continued. In the second step, the temperature was ramped to 170 °C over 25 min and held for 20 min to dissolve any precipitated fluorides.

Following the two-step digestion, the solutions were made up to 50 mL with de-ionized (DI) water. Final acid concentrations were as follows: 16% HNO_3, 2% HCl, 2% H_2O_2, and 0.8% H_3BO_3. The 2% HF included in the digestion mix was neutralized by the addition of the H_3BO_3. The concentration of total dissolved solids in the final digests analyzed was approximately 0.3% (3000 ppm), including sediment matrix (~0.2%) and boron (0.14%). Samples containing 0.3% TDS are easily within the 3% limit that the 7800 ICP-MS can handle routinely.

Each sediment CRM was spiked before the two-step microwave digestion procedure. The final concentration of each spiked element was 50 ppb in the 50 mL final digests analyzed.

The sample tubes were loaded on the Agilent SPS 4 autosampler ready for analysis.

Calibration standards and QC sample preparation

All standards were diluted in an acid mix comprising 16% HNO_3, 2.0% HCl, and 0.8% H_3BO_3. The acid matrix is closely matched to the acid composition of the final sample digests. There was no need to add HF to the standards because any HF remaining after the digestion would be neutralized by H_3BO_3.

Initial calibration was performed using a six-point calibration curve including calibration blank. The concentrations of the calibration standards are shown in Figure 2.

The ISTD solution was added to the sample flow using the standard online ISTD mixing connector.

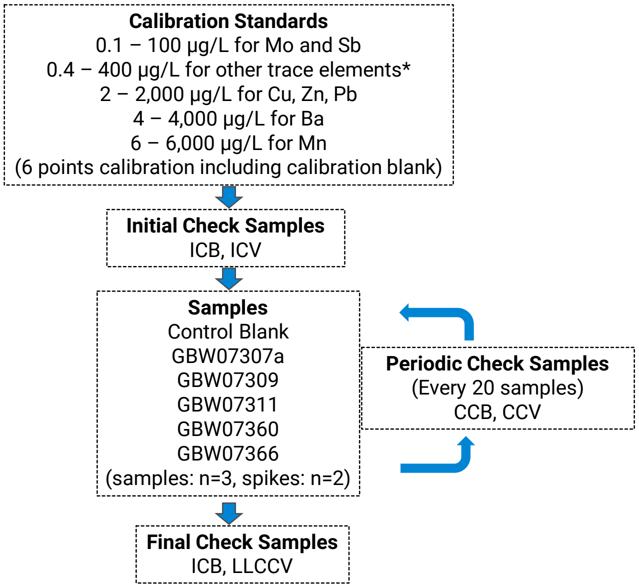

Figure 2. Flow diagram showing samples, calibration standards, and check samples analyzed in sequence. The "Samples" block was repeated continuously with automatic insertion of the "Periodic Check Samples" block after every 20 sample runs.

Other trace elements included in the analysis were Be, V, Cr, Co, Ni, As, Ag, Cd, and Tl.

Instrumentation

All measurements were performed using an Agilent 7800 ICP-MS fitted as standard with HMI, Ni interface cones, and ORS^4 collision cell operating in He mode. An Agilent SPS 4 autosampler was used for introduction of all standards and samples to the ICP-MS. The use of H_3BO_3 to neutralize the HF during the digestion meant that an “inert” (HF resistant) sample introduction kit was not required. As a result, the standard glass/quartz sample introduction system was used.

The instrument operating parameters were loaded from the "high matrix" Preset Method in the ICP-MS MassHunter software, allowing the analyst to create a new batch method quickly. In this study, all the plasma parameters listed in Table 1 were automatically loaded by selecting “HMI-4” in the batch conditions.

Correction equations for certain isotopes (^{6}Li, ^{115}In, and ^{208}Pb) are set by default in the preset method. These equations correct for direct elemental overlaps from natural ^{6}Li on the enriched ^{6}Li often used as an internal standard, and ^{115}Sn on ^{115}In. In the case of Pb, the equation—which sums the signal from the 3 main isotopes at mass 206, 207, and 208—is used to eliminate errors due to natural isotopic variability. The Technical Stipulation for China Soil method allows the use of additional mathematical correction equations, which were traditionally used to correct for spectral interferences in ICP-MS. However, He mode on the 7800 removes common polyatomic ions effectively, regardless of the sample matrix, so these traditional interference correction equations were not needed.

Table 1. ICP-MS operating parameters*.

Parameter	No gas mode	He mode
Plasma mode	HMI-4	
RF power (W)	1600	
Nebulizer gas flow (L/min)	0.60	
Dilution gas flow (L/min)	0.35	
Lens tune	Autotune	
Cell gas flow (mL/min)	0.0	4.5
Energy discrimination (V)	5.0	

** Shaded parameters are defined in the method and HMI-4 plasma presets; all parameters were automatically optimized during start-up and autotuning.*

Results and Discussion

Calibration

The QC requirements defined in the Technical Stipulation for China Soil method state that the R value for all calibration curves should be greater than 0.999. As indicated by the four representative calibration curves shown in Figure 3, excellent linearity was achieved for major elements and trace elements. In all cases, the R value was greater than 0.9999, exceeding the method requirement.

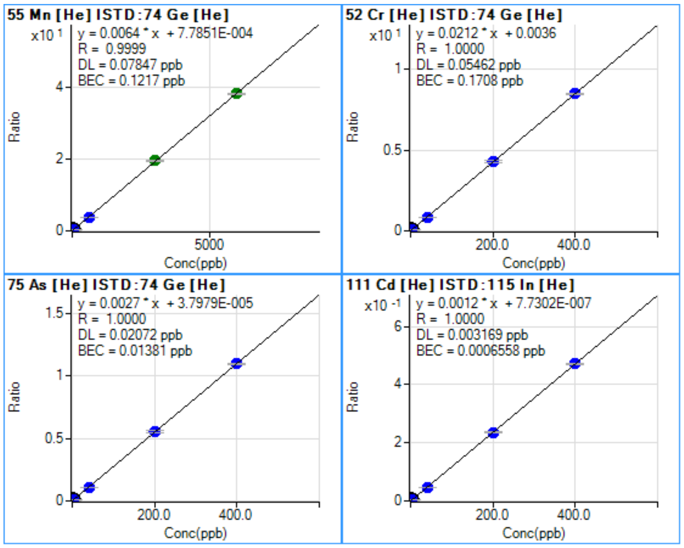

Figure 3. Representative calibration curves for major element (Mn) and trace elements (Cr, As, and Cd).

Detection Limits (DLs)

The three sigma DLs shown in Table 2 were calculated from 10 replicate measurements of the matrix-matched calibration blank. The blank was prepared with the same level of HNO_3, HCl, and H_3BO_3 as was present in the final sample solutions. In this analysis, for optimum detection limits, Be was acquired in no gas mode, together with the internal standard ^{6}Li. The Technical Stipulation for China Soil method specifies a very low MDL for Be of 0.003 mg/kg (ppm), which was easily achieved using the 7800 ICP-MS. All the other elements were acquired in He mode. The DLs ranged from 0.001 to 0.228 µg/L in the digest solution, which equates to 0.001 to 0.114 mg/kg (ppm) in the sediment.

Table 2. Three sigma method detection limits.

Element	Gas mode	ISTD	Integration time (sec)	3 sigma DL (µg/L)	3 sigma DL in sediment (mg/kg)	China method required MDLs (mg/kg)
9 Be	No gas	6 Li	1.0	0.004	0.002	0.003
51 V	He	74 Ge	0.5	0.020	0.010	0.030
52 Cr	He	74 Ge	0.5	0.054	0.027	0.400
55 Mn	He	74 Ge	0.3	0.078	0.039	(no value for Mn)
59 Co	He	74 Ge	0.3	0.005	0.003	0.007
60 Ni	He	74 Ge	0.3	0.057	0.029	0.300
63 Cu	He	74 Ge	0.5	0.049	0.025	0.600
66 Zn	He	74 Ge	0.3	0.228	0.114	2.00
75 As	He	74 Ge	1.0	0.021	0.011	(no value for As)
95 Mo	He	103 Rh	1.0	0.011	0.006	0.100
107 Ag	He	103 Rh	0.3	0.011	0.006	(no value for Ag)
111 Cd	He	115 In	1.0	0.003	0.002	0.030
121 Sb	He	115 In	1.0	0.001	0.001	(no value for Sb)
135 Ba	He	115 In	0.1	0.105	0.053	(no value for Ba)
205 Tl	He	185 Re	1.0	0.005	0.003	0.020
208 Pb	He	185 Re	0.9* (0.3x3)	0.013	0.006	2.00

** Pb is measured as the sum of the three most abundant isotopes, 206, 207, and 208.*

ISTD recoveries

In total, 109 solutions were analyzed over a period of 7 hours. From the list of internal standard elements recommended in the soil survey method, the elements ^{6}Li, ^{74}Ge, ^{103}Rh, ^{115}In, and ^{185}Re were used in this study.

All the ISTD recovery measurements were within the control limits of ± 30% specified in the method, as shown in Figure 4.

Because of the high matrix tolerance of the 7800 ICP-MS with HMI, there was very little variability in the ISTD signals from sample to sample throughout the run. Also, there was no overall signal drift during the sequence and no divergence in the signals for low- and high-mass ISTD elements. This excellent ISTD stability indicates that the 7800 ICP-MS was able to decompose the variable sample matrices very effectively, and no significant matrix deposition occurred on the interface during the entire sequence.

It is very useful for all the ISTD signals to be consistent, so analysts can easily substitute a different element if one of the normal ISTD elements is present in the samples or is a required analyte. This is increasingly likely, as several normal ICP-MS ISTD elements are used in high technology manufacturing industries and are becoming of interest as emerging environmental contaminants.

For labs analyzing very high sample numbers, higher sample throughput may be required. The 7800 ICP-MS can be fitted with the optional Integrated Sample Introduction System (ISIS 3) valve injection system (*2*, *3*). ISIS 3 uses discrete sampling to shorten the analysis time by overlapping the acquisition with the sample uptake and rinse times. This allows the analysis time to be reduced from 4 min/sample to around 1 min/sample.

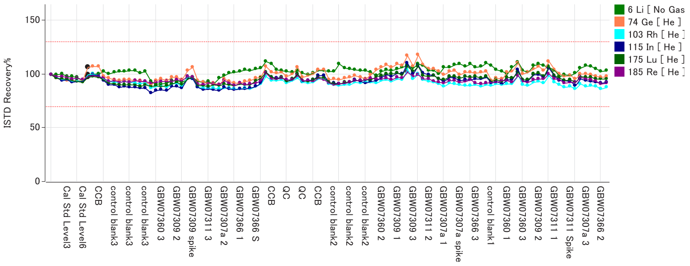

Figure 4. ISTD stability during the analysis of a total of 109 solutions measured over a 7-hour run. ISTD recoveries for all samples have been normalized to the calibration blank. Due to limited space, not all sample names are shown.

Recoveries of QC samples

The standard used to generate the mid point of the calibration curve was measured as a continuing calibration verification (CCV) standard. The CCV was included in the Periodic Sample Block measured automatically after every 20 samples, as stipulated in the method. According to the method requirements, the CCV recovery must be within ±10%, with a CCV recovery outside this limit triggering a recalibration. Figure 5 shows that all the elements met the criteria, without the need to recalibrate throughout the 7-hour sequence.

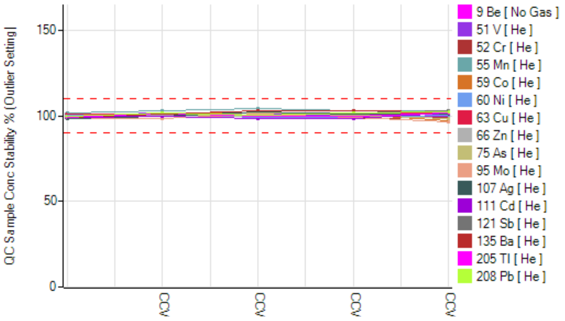

Figure 5. Continuing calibration verification (CCV) recoveries over the course of the 7-hour sequence.

The Technical Stipulation for China Soil method also requires that the Low Level Initial Calibration Verification (LLICV) standard should be measured at the end of the sequence. The required control limits for the LLICV are ±30% of the actual value. Table 3 shows all the recoveries were easily within the limits.

Table 3. Measured concentrations and recoveries of the lowest calibration standard, repeated as an unknown sample at the end of the sequence. In the Technical Stipulation for China Soil method, recoveries should be within ±30% of the actual concentration.

Element	Measured LLICV concentration (ppb)	Actual LLICV concentration (ppb)	Recovery (%)
9 Be	0.461	0.4	115
51 V	0.377	0.4	94
52 Cr	0.367	0.4	92
55 Mn	5.744	6	96
59 Co	0.371	0.4	93
60 Ni	0.328	0.4	82
63 Cu	1.846	2	92
66 Zn	2.134	2	107
75 As	0.314	0.4	79
95 Mo	0.095	0.1	95
107 Ag	0.399	0.4	100
111 Cd	0.444	0.4	111
121 Sb	0.097	0.1	97
135 Ba	4.148	4	104
205 Tl	0.471	0.4	118
208 Pb	2.044	2	104

Spike recoveries

Each CRM was spiked before microwave digestion. The final spike concentration for each analyte was 50 ppb. In accordance with the method requirements, the spike recovery limit was set to ±20%. If the measured spike concentration falls outside the limit, the sample must be diluted and analyzed again. Table 4 shows Matrix Spike (sample 1) and Matrix Spike Duplicate (sample 2) results for CRM GBW07307a, together with the calculated recoveries and the difference between the two measured results. As the concentration of Mn, Zn, Ba, and Pb in the CRM was much higher than the 50 ppb spike, no spike recoveries were calculated for these elements. The CRM recoveries in Table 5 show that the method can analyze these high concentration elements with good accuracy.

Recoveries for all other elements were within ±10% of the true spike level, demonstrating that the accuracy of the method easily meets the Chinese method requirements. The relative percent difference between the recoveries of the two spiked samples was calculated. All elements met the limit of 20% defined in the method. The results in Table 4 and 5 show that the 7800 ICP-MS can accurately measure multiple elements in high matrix samples across a wide dynamic range.

Table 4. Concentrations, recoveries, and deviations of two samples of GBW07307a CRM spiked at 50 ppb.

Element	Unspiked conc. (ppb)	Spiked sample 1 (ppb)	Spiked sample 2 (ppb)	Sample 1 spike recovery (%)	Sample 2 spike recovery (%)	Relative % difference (%)
9 Be	3.20	53.1	51.4	100	96	3.5
51 V	154	207	201	105	93	12
52 Cr	88.5	140	137	103	97	6
55 Mn	1790	N/A*	N/A*	-	-	
59 Co	29.6	79.3	77.1	99	95	4.5
60 Ni	46.7	96.1	94.7	99	96	2.9
63 Cu	46.8	96.8	93.4	100	93	7
66 Zn	1690	N/A*	N/A*	-	-	-
75 As	26.4	77.3	76.0	102	99	2.6
95 Mo	1.58	53.0	51.7	103	100	2.5
107 Ag	2.40	52.2	51.5	100	98	1.3
111 Cd	11.9	62.6	62.8	101	102	0.4
121 Sb	4.71	57.9	57.3	106	105	1.1
135 Ba	806	N/A*	N/A*	-	-	-
205 Tl	0.75	49.8	50.0	98	99	0.4
208 Pb	1184	N/A*	N/A*	-	-	-

** Spike level of 50 ppb was not high enough relative to the concentration in the unspiked sample.*

CRM recoveries

The five certified reference samples were prepared in triplicate and analyzed repeatedly in the “Samples” block (see Figure 2). The results in Table 5 show the mean measured concentrations in the sediment digests, and the mean recoveries compared to the certified values. The results for all elements were in good agreement with the certified values. Using closed vessels during the digestion, even volatile elements such as As and Sb showed good recoveries.

Table 5. Mean concentrations in sediment CRMs as ppb in the solutions analyzed and as mg/kg in the original CRM (corrected for dilution). Certified values (mg/kg) are included for each CRM, and mean recoveries (%) are shown for all certified elements in the five CRMs. N=3.

	GBW07307a				GBW07309				GBW07311			
(n=3)	Measured in solution (ppb)	Measured in sediment (mg/kg)	Certified value (mg/kg)	Mean recovery (%)	Measured in solution (ppb)	Measured in sediment (mg/kg)	Certified value (mg/kg)	Mean recovery (%)	Measured in solution (ppb)	Measured in sediment (mg/kg)	Certified value (mg/kg)	Mean recovery (%)
9 Be	3.20	1.6 ± 0.4	1.6 ± 0.1	100	3.62	1.8 ± 0.0	1.8 ± 0.3	101	58.01	29 ± 1	26 ± 3	112
51 V	154	77 ± 9	77 ± 4	100	183.3	92 ± 1	97 ± 6	94	81.47	41 ± 2	47 ± 3	87
52 Cr	88.5	44 ± 5	43 ± 1	103	152.7	76 ± 1	85 ± 7	90	71.47	36 ± 2	40 ± 3	89
55 Mn	1790	896 ± 100	886 ± 25	101	1222	611 ± 2	620 ± 20	99	4880	2440 ± 124	2490 ± 84	98
59 Co	29.6	14.8 ± 2.1	15.2 ± 0.7	98	25.46	12.7 ± 0.1	14.4 ± 1.2	88	14.61	7.3 ± 0.5	8.5 ± 0.8	86
60 Ni	46.7	23.3 ± 3.6	22.0 ± 0.6	106	60.13	30 ± 0	32 ± 2	94	25.85	12.9 ± 0.7	14.3 ± 1.0	90
63 Cu	46.8	23.4 ± 3.6	22.5 ± 1.0	104	62.74	31 ± 0	32 ± 2	98	149.3	75 ± 4	79 ± 3	94
66 Zn	1690	844 ± 54	780 ± 19	108	145.0	73 ± 1	78 ± 4	93	719.2	360 ± 5	373 ± 14	96
75 As	26.4	13.2 ± 1.6	11.3 ± 1.0	117	18.09	9.0 ± 0.2	8.4 ± 0.9	108	354.5	177 ± 10	188 ± 13	94
95 Mo	1.58	0.79 ± 0.08	0.82 ± 0.05	96	1.31	0.66 ± 0.02	0.64 ± 0.11	103	13.50	6.8 ± 0.0	5.9 ± 0.6	115
107 Ag	2.40	1.20 ± 0.15	1.20 ± 0.08	100	0.16	0.082 ± 0.006	0.089 ± 0.010	92	6.06	3.0 ± 0.1	3.2 ± 0.4	95
111 Cd	11.9	6.0 ± 0.4	5.6 ± 0.6	107	0.60	0.29 ± 0.04	0.26 ± 0.04	113	4.42	2.2 ± 0.0	2.3 ± 0.2	96
121 Sb	4.71	2.4 ± 0.8	2.1 ± 0.2	112	1.91	0.95 ± 0.01	0.81 ± 0.15	118	30.14	15.1 ± 0.6	14.9 ± 1.2	101
135 Ba	806.0	403 ± 50	437 ± 12	92	864.3	432 ± 5	430 ± 18	101	491.0	245 ± 3	260 ± 17	98
205 Tl	0.75	0.37 ± 0.03	0.45 ± 0.07	83	0.89	0.44 ± 0.02	0.49 ± 0.08	90	5.47	2.7 ± 0.05	2.9 ± 0.4	105
208 Pb	1184	592 ± 52	555 ± 19	107	44.10	22 ± 0	23 ± 3	96	1295	648 ± 10	636 ± 22	106

	GBW07360				GBW07366			
(n=3)	Measured in solution (ppb)	Measured in sediment (mg/kg)	Certified value (mg/kg)	Mean recovery (%)	Measured in solution (ppb)	Measured in sediment (mg/kg)	Certified value (mg/kg)	Mean recovery (%)
9 Be	5.90	3.0 ± 0.3	2.9 ± 0.3	102	4.88	2.4 ± 1.0	2.4 ± 0.1	102
51 V	92.26	46 ± 2	49 ± 3	94	190.5	95 ± 4	101 ± 3	94
52 Cr	61.41	31 ± 2	35 ± 2	88	127.4	64 ± 2	72 ± 3	88
55 Mn	2925	1460 ± 3	1490 ± 4	98	2071	1040 ± 22	1030 ± 3	101
59 Co	16.49	8.2 ± 0.4	9.4 ± 0.2	88	25.36	12.7 ± 0.2	14.4 ± 0.5	88
60 Ni	26.01	13.0 ± 0.9	14.4 ± 0.7	90	52.37	26 ± 1	29 ± 1	90
63 Cu	50.71	25.4 ± 0.9	26.5 ± 1.0	96	908.9	454 ± 21	483 ± 20	94
66 Zn	1099	550 ± 16	579 ± 17	95	1658	829 ± 7	874 ± 19	95
75 As	83.65	42 ± 0	43 ± 4	97	582.6	291 ± 9	304 ± 20	96
95 Mo	3.28	1.6 ± 0.1	1.6 ± 0.2	102	3.25	1.62 ± 0.01	1.56 ± 0.20	104
107 Ag	1.60	0.80 ± 0.04	0.74 ± 0.14	108	4.30	2.2 ± 0.1	2.1 ± 0.3	102
111 Cd	8.54	4.3 ± 0.2	4.3 ± 0.5	99	9.55	4.8 ± 0.1	4.8 ± 0.5	99
121 Sb	4.74	2.4 ± 0.3	2.0 ± 0.2	118	53.81	27 ± 1	25 ± 4	108
135 Ba	1228	614 ± 24	623 ± 18	99	1194	597 ± 2	590 ± 10	101
205 Tl	2.68	1.34 ± 0.04	1.38 ± 0.17	97	1.97	0.98 ± 0.02	1.05 ± 0.08	94
208 Pb	687.0	344 ± 13	341 ± 15	101	267.0	133 ± 2	126 ± 5	106

Soils

To further demonstrate the applicability of the 7800 ICP-MS, multiple elements were analyzed in eight soil CRMs obtained from NCS, China. The data was acquired using a method based on the one used in this work but run in a different laboratory. The samples were digested using an Ethos One microwave system (Milestone, USA) and analyzed using a different Agilent 7800 ICP-MS. The results in Table 6 confirm that the ICP-MS method using the 7800 ICP-MS with HMI can also be used for the accurate analysis of soil sample digests.

Table 6. Measured concentrations (ppm) for eight soil CRMs, including certified element concentrations, and % recovery.

	GSS-9			GSS-10			GSS-11			GSS-12		
	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Be	2.2	2.2 ± 0.1	98	2.5	2.4 ± 0.1	104	2.24	2.25 ± 0.08	100	2.04	2.04 ± 0.06	100
V	89	90 ± 12	99	78	74 ± 3	105	73	74 ± 2	99	88	86 ± 4	103
Cr	75	75 ± 5	99	57	58 ± 2	98	57	59 ± 3	96	59	59 ± 2	100
Mn	533	520 ± 24	102	687	681 ± 13	101	567	572 ± 14	99	758	774 ± 19	98
Co	13	14 ± 2	94	11.9	11.7 ± 0.5	102	11.0	11.6 ± 0.4	94	12.3	12.6 ± 0.3	98
Ni	35	33 ± 3	107	28	26 ± 1	108	26.2	25.4 ± 1.3	103	34	32 ± 1	106
Cu	24	25 ± 3	94	17	19 ± 1	90	19	21.4 ± 1.2	89	27	29 ± 1	93
Zn	59	61 ± 5	97	57	60 ± 4	95	60	65 ± 5	92	74	78 ± 5	95
Mo	0.3	0.4 ± 0.1	82	0.48	0.52 ± 0.04	92	0.57	0.60 ± 0.04	95	1.02	0.96 ± 0.06	106
Cd	0.1	0.10 ± 0.02	107	0.126	0.105 ± 0.013	120	0.131	0.125 ± 0.012	105	0.16	0.15 ± 0.02	106
Sb	1.35	1.1	123	1.15	0.94	122	1.00	0.82	122	1.47	1.17	125
Ba	494	520 ± 43	95	512	613 ± 12	84	542	634 ± 10	85	444	492 ± 20	90
Tl	0.5	0.6 ± 0.1	89	0.60	0.58 ± 0.05	103	0.57	0.62 ± 0.02	91	0.46	0.51 ± 0.04	90
Pb	23	25 ± 3	93	24	22 ± 2	110	25.0	24.7 ± 1.4	101	18	19 ± 2	96

	GSS-13			GSS-14			GSS-16			GSS-27		
	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Be	2.01	1.9 ± 0.05	106	2.53	2.44 ± 0.06	103	3.6	3.8 ± 0.3	96	2.3	2.3 ± 0.1	102
V	74	74 ± 2	100	87	86 ± 2	101	104	105 ± 4	99	122	120 ± 6	102
Cr	62	65 ± 2	95	69	70 ± 3	99	66	67 ± 3	98	94	92 ± 4	102
Mn	553	580 ± 12	95	657	688 ± 15	96	424	441 ± 20	96	938	956 ± 37	98
Co	10.9	11.3 ± 0.5	97	14.5	14.6 ± 0.7	99	13.1	13.6 ± 0.6	96	18.3	19 ± 0.6	96
Ni	29.4	28.5 ± 1.2	103	35	33 ± 2	105	29.4	27.4 ± 0.9	107	46	43 ± 2	107
Cu	19.3	21.6 ± 0.8	89	25.9	27.4 ± 1.1	95	30	32 ± 2	93	53	54 ± 2	98
Zn	60	65 ± 3	92	92	96 ± 3	96	95	100 ± 8	95	118	127 ± 4	93
Mo	0.42	0.48 ± 0.03	88	0.60	0.65 ± 0.06	92	1.27	1.15 ± 0.07	110	0.77	0.84 ± 0.11	92
Cd	0.14	0.13 ± 0.01	109	0.21	0.20 ± 0.02	105	0.29	0.25 ± 0.02	116	0.55	0.59 ± 0.04	93
Sb	1.20	0.99	121	0.94	0.81	116	2.15	1.9	113	1.42	1.21 ± 0.04	117
Ba	433	500 ± 15	87	507	608 ± 13	83	346	411 ± 18	84	484	496 ± 15	98
Tl	0.47	0.52 ± 0.05	91	0.59	0.63 ± 0.03	93	1.02	1.12 ± 0.08	91	0.56	0.67 ± 0.07	83
Pb	21.2	21.6 ± 1.2	98	32	31 ± 1	102	62	61 ± 2	102	41	41 ± 2	99

Conclusions

This study shows that sediment sample digests can be analyzed routinely using the Agilent 7800 ICP-MS with HMI and He mode. The HMI aerosol dilution system allows variable high matrix samples to be introduced to the instrument over extended periods without degrading sensitivity or stability. The accurate quantification of a wide range of analyte concentrations typically found in soils and sediments was possible using He mode to remove polyatomic interferences.

The microwave digestion sample preparation method was optimized to digest 30 sediment samples simultaneously. The digestion method enabled all elements, including volatile analytes such as As and Sb, to be measured with good accuracy, as shown by the spike recovery results. HMI aerosol dilution minimized the need for liquid dilution of the samples, so the vials used for sample preparation could be loaded directly in the autosampler. HMI shortens the sample preparation time, reduces the risks of contamination or human errors, and improves method DLs by allowing lower dilutions to be applied.

ICP-MS MassHunter software provides easy-to-follow method setup and data analysis/reporting tools to help the operator generate new methods and process results. A preset method was used in this study to simplify the development of the method, operation of the method, and interpretation of the data.

Reliable routine analysis of the environmental samples targeted in the Technical Stipulation for China Soil method can be carried out quickly and easily using the 7800 ICP-MS.

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Printed in the USA, October 19, 2018
5994-0309EN

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