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Simple and Reliable Soil Analysis using the Agilent 7800 ICP-MS with ISIS 3

Application Environmental



Introduction

Regulations concerning activities such as land use, waste discharge consents, and remediation of former industrial sites require routine monitoring of environmental samples to identify and confirm the levels of heavy metal pollution. US Environmental Protection Agency (EPA) Method 6020A (Rev 4, February 2007) provides guidance on the determination of over 60 elements ranging from major to ultratrace concentration levels in various types of environmental samples. Typical samples include surface and groundwaters, as well as high matrix samples such as industrial wastes, digested soils, sludges, sediments, and other solid wastes.

Fast, simple-to-use instrumentation with multi-element analysis capability and good long-term stability is required for the routine analysis of large numbers of samples. ICP-MS possesses all these desirable characteristics, but it is considered challenging to analyze large batches of variable, high matrix samples using ICP-MS, due to the accumulation of undissociated sample matrix material on the ICP-MS interface. This accumulation affects the stability of the analysis and causes long-term drift. Sample dilution can be used to reduce matrix loading, but conventional liquid dilution adds to the sample preparation overhead. It can also



contribute to contamination from the diluent reagents and the additional sample handling steps. Furthermore, sample dilution means that lower instrumental detection limits are required to maintain the method detection limits.

The Agilent 7800 ICP-MS is highly suited to EPA Method 6020A compliant analysis of environmental samples. The 7800's standard equipment includes the High Matrix Introduction (HMI) system and fourth-generation Octopole Reaction System (ORS⁴) collision/reaction cell (CRC) technology. HMI improves the robustness of the ICP-MS plasma by applying a selected and precisely calibrated aerosol dilution factor to reduce matrix loading on the plasma and interface. This approach minimizes any signal variation due to changes in the matrix level, and allows the analysis of high matrix samples over extended periods with good stability. The ORS⁴ cell of the 7800 is optimized for helium collision mode (He mode), offering a simpler approach to controlling interferences compared to selective reaction chemistry. He mode uses kinetic energy discrimination (KED) to reduce the transmission of all common matrix-based polyatomic interferences. This attenuation removes or significantly reduces the contribution that the polyatomic ions make to the analyte signals, improving accuracy for the interfered elements. The 7800 ICP-MS also has the high sensitivity and wide dynamic range (10 orders) required to meet EPA 6020A quality control (QC) limits, even when sample preparation methods lead to relatively large dilution factors being used.

Agilent's powerful and multifunctional ICP-MS MassHunter software for the 7800 simplifies method development, using extensive auto-optimization and Preset Method templates to quickly and easily create new batches. The software also includes sample and QC report templates, and the data batch display provides flexible QC and internal standard (ISTD) recovery graphs. If any values exceed the set limits, they are automatically flagged in the data table. Ease of instrument setup and operation is further enhanced by the detailed standard operating procedure (SOP) template that is supplied with the 7800. The SOP guides new users through the steps required to prepare the system and define methods ready for routine use.

To perform high speed, automated discrete sampling analysis, the 7800 can be fitted with the optional Integrated Sample Introduction System (ISIS 3). ISIS 3 uses a high-flow piston pump to quickly load the sample into the loop, ready for injection. Discrete sampling speeds up the overall analysis by washing out the sample probe and autosampler tubing during the data acquisition step. As a result, ISIS 3 shortens the analysis time by half compared with conventional sample introduction, while minimizing any carryover from previous samples. This study describes the analysis of soils and sediments according to EPA Method 6020A using the Agilent 7800 ICP-MS with ISIS 3 and SPS 4 autosampler.

Experimental

Standard and sample preparation

Calibration standards, spikes, and all QC standards, except the ICV, were prepared from Agilent's Environmnetal calibration standard 5183–4688 fortified with the addition of single element standards for AI, Hg, Na, K, Ca, Se, V, Cr, Mn, Zn, and Pb (1000 μ g/mL, obtained from Kanto Chemicals, Japan). The single element additions were to allow Hg to be included in the mixed calibration standards, and to increase the concentration of the major elements to more closely match the concentrations in the sample types – soil and sediment – of interest. The ICV was prepared from Agilent's initial calibration verification standard 5183–4682 plus the addition of single element standards for AI and Hg, for the same reason as previously outlined.

The certified reference materials (CRMs) used in the analysis were NIST 1640a Natural Water (NIST, Gaithersburg MD), River Sediment A, River Sediment B, Estuarian Sediment, Soil A, and Soil B (all from High Purity Standards (HPS), Charleston SC, USA).

The HPS soil and sediment CRMs are synthetic solutions prepared at 1 g/100 mL in 4% $HNO_{3'}$ to simulate the typical elemental composition of an acid digest of each sample type. The samples were further diluted 10x and 50x, to illustrate the capability of the 7800 ICP-MS to deliver accurate results across a range of sample matrix levels and analyte concentrations from ultratrace to major elements. The maximum matrix level was 0.1% total dissolved solids (TDS), which is easily within the limit that the 7800 can handle routinely. However, the high sensitivity of the 7800 instrument allows EPA 6020A QC requirements to be met for these diluted sample matrix levels. In addition, the use of HMI minimized the potential for signal instability due to matrix deposition, while also reducing maintenance requirements.

The sample diluent used was 1.0% HNO₃ and 0.5% HCl. The addition of HCl to the final acid mix ensured stability of certain elements such as Hg. The calibration standards were prepared in the same acid mix.

The Internal Standard (ISTD) solution used (Agilent 5183– 4681) contained 1 ppm ⁶Li, Sc, Ge, Y, In, Tb, and Bi. The ISTD solution was automatically added to the carrier/sample flow via the ISIS 3's seventh port, giving approximately a 1:15 dilution into the solution being transferred to the nebulizer. Each CRM was prepared with two dilution factors:

- NIST 1640a was prepared undiluted and 10x diluted.
- The soil and sediment CRMs were prepared at 10x and 50x dilutions of the CRM solutions.

The spike additions for the Matrix Spike (MS) and Matrix Spike Duplicate (MSD) samples were added to the 10x diluted CRMs. Trace elements were spiked at 10 ppb, mineral elements (Na, Mg, Al, K, Ca, and Fe) at 1000 ppb, Zn at 100 ppb, Ba at 500 ppb, and Hg at 0.2 ppb.

The analytical sequence of calibrants, QC solutions, and samples is shown in Figure 1. The sample block was analyzed repeatedly with automatic insertion of the Periodic QC block after every 10th sample run.



Figure 1. Analytical sequence. The "Samples" block was run repeatedly with automatic insertion of the "Periodic QC" block after every 10 sample runs. Total number of analyses over the course of the sequence was 389.

Instrumentation

All measurements were performed using an Agilent 7800 ICP-MS equipped with HMI, Ni interface cones, and ORS⁴ CRC as standard. Sample delivery utilized the optional ISIS 3 and the Agilent SPS 4 autosampler. To support the high solution pump speeds used with ISIS 3, the autosampler was fitted with an optional large-bore (1.0 mm id) sample probe rather than the standard probe with 0.5 mm id.

The acquisition parameters were based on the preset method "EPA 6020", simplifying method setup by predefining analytical parameters such as analytes, acquisition masses, and integration times. The plasma conditions and other instrument operating parameters were automatically optimized using the preset plasma mode "HMI-4". The plasma preset automates the setting of key plasma parameters to ensure reliable and reproducible conditions for analyzing the target sample types. This simple setup process allows busy analysts to create a method quickly and confidently. It also ensures that operating conditions are appropriate and consistent even when batch setup and acquisition is performed by multiple operators.

Any custom requirements (such as autosampler-specific uptake and rinse settings, addition of extra analytes, or modification of specific acquisition parameters) can be applied to the batch, which may then be saved as a new method template for future use. In this study, the plasma mode parameters (RF power, nebulizer gas flow, and dilution gas flow) were loaded from the "HMI-4" plasma preset (Table 1), and the lens voltages were optimized automatically using autotune. The helium cell gas flow was set to 4.3 mL/ min for optimum sensitivity for all analytes.

ISIS 3, which is described elsewhere [1, 2], has many practical benefits for this application, including:

- Solution is delivered to the nebulizer at a constant flow rate. This delivery eliminates the need for stabilization after high speed uptake and reduces the run time by as much as a minute per sample.
- Sample uptake and analysis are separated, so the system can begin rinsing the sample uptake tubing and loop before the previous analysis is finished. This capability reduces the run time by as much as a minute.
- Sample is delivered to the plasma only during the actual data acquisition step; at all other times, a clean blank or rinse solution is being nebulized. This approach results in a 3–5x reduction in the amount of sample matrix reaching the instrument. By minimizing matrix deposition on the interface, the need for routine cleaning and maintenance is decreased.
- ISIS 3 includes a 3-way valve that enables a continuous, automated workflow – from system startup and optimization to sample measurement and data analysis – without the need to manually change the tubing or connections.
- Fast sample transfer and washout are achieved by close coupling of the ISIS 3 valve, which is positioned next to the nebulizer. This layout reduces the sample tubing length and the required rinse time.
- ISIS 3 loads the loop and injects the sample through the same port of the switching valve, by reversing the flow through the loop (Figure 3). This function reduces the possibility of poor repeatability or sequence errors if the sample loop is not filled completely.

Using the operating parameters shown in Table 2, sample analysis using ISIS 3 took only 92 seconds, including two cell modes. This time is about half the time of a conventional analysis without discrete sampling [3].

Table 1. ICP-MS operating parameters.

| ICP-MS parameter | No gas mode He mode | | | |
|---|---------------------------------------|----------|--|--|
| Plasma mode | HMI-4 | | | |
| RF power (W) | 16 | 00 | | |
| Spray chamber temp (°C) | : | | | |
| Sampling depth (mm) | 10 | | | |
| Nebulizer gas flow (L/min) | 0.60 | | | |
| Dilution gas flow (L/min) | 0.35 | | | |
| Lens tune | Autotune | | | |
| Cell gas flow (mL/min) | 0.0 (predefined) 4.3 | | | |
| Energy discrimination (V) | 5.0 (pre | defined) | | |
| Number of elements | 1 analyte, 1 ISTD 25 analytes, 5 ISTI | | | |
| Data acquisition time for 3 replicates, including cell gas switching time (s) | 46.5 | | | |

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

 Table 2. ISIS 3 operating parameters.

| ISIS 3 parameter | Setting | | | |
|--------------------------|-----------------|----------------|--|--|
| Loop volume (µL) | 1000 | | | |
| | Time uptake (s) | Pump speed (%) | | |
| Sample load | 7 | 36 | | |
| Stabilization | 23 | 5 | | |
| Probe rinse | 25 | 5 | | |
| Probe rinse 1 | 5 | 80 | | |
| Probe rinse 2 | 10 | 5 | | |
| Optional loop probe wash | 7 | 60 | | |
| Optional loop wash | 1 5 | | | |
| Total time per sample* | 92 se | conds | | |

*Includes autosampler probe movement and overlapping acquisition time.



Figure 2. Signal intensity during ISIS 3 operation.



Inject



Figure 3. Overview of ISIS 3 operation, showing valve in Load (top) and Inject (bottom) positions.

Results and Discussion

Method detection limits

Three sigma Method Detection Limits (MDLs) were calculated from 10 replicates of the low standard (trace elements: 0.1 ppb; mineral elements: 10 ppb; and Hg: 0.01

ppb) and the results are shown in Table 3. While all regulated elements can be measured successfully using a single He mode on the 7800, for optimum detection limits, Be (and ⁶Li ISTD) was acquired in no gas mode in this work. All the other elements were acquired in He mode. Integration times were based on the EPA 6020 preset method, with increased times for As and Se to optimize DLs for these trace analytes. The small volume, octopole-based CRC of the 7800 means that cell gas mode changes can be achieved with minimal switching time of only a few seconds. As a result, the two-step, triplicate acquisition was still compatible with the short stable signal time available with discrete sampling, illustrated in Figure 2. For most elements, MDLs between 0.01 and 0.1 μ g/L (ppb) were achieved.

 Table 3. Three sigma method detection limits (MDLs) in the sample solutions as analyzed, calculated from 10 replicates of the low-level calibration standard.

| Element and mass number | Gas mode | Integration time (s) | 3 sigma MDL (ppb) | |
|----------------------------|----------|-------------------------|----------------------|--|
| 9 Be | No gas | 0.3 | 0.013 | |
| 23 Na | He | 0.1 | 2.79 | |
| 24 Mg | He | 0.1 | 1.02 | |
| 27 AI | He | 0.5 | 0.252 | |
| 39 K | He | 0.1 | 3.54 | |
| 44 Ca | Не | 0.2 | 4.23 | |
| 51 V | He | 0.3 | 0.021 | |
| 52 Cr | He | 0.3 | 0.069 | |
| 55 Mn | He | 0.3 | 0.033 | |
| 56 Fe | Не | 0.3 | 0.419 | |
| 59 Co | Не | 0.3 | 0.015 | |
| 60 Ni | He | 0.3 | 0.069 | |
| 63 Cu | Не | 0.3 | 0.019 | |
| 66 Zn | Не | 0.3 | 0.169 | |
| 75 As | He | 1.0 | 0.031 | |
| 78 Se | He | 2.0 | 0.202 | |
| 95 Mo | He | 0.3 | 0.021 | |
| 107 Ag | He | 0.3 | 0.015 | |
| 111 Cd | He | 1.0 | 0.020 | |
| 121 Sb | He | 0.1 | 0.017 | |
| 137 Ba | He | 0.3 | 0.059 | |
| 201 Hg | He | 1.0 | 0.003 | |
| 205 TI | Не | 0.3 | 0.014 | |
| 206, 207, 208 Pb | Не | 0.3 (0.1x3)* | 0.016 | |
| 232 Th | Не | 0.1 | 0.017 | |
| 238 U | Не | 0.1 | 0.020 | |

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

LLICV and ICV concentrations and recoveries

EPA 6020A (Feb 2007) requires a Low Level Initial Calibration Verification (LLICV) check at approximately the method reporting limit. The results for the LLICV and Initial Calibration Verification (ICV) check solutions are shown in Table 4.

The recommended control limits of LLICV and ICV are $\pm 30\%$ and $\pm 10\%$ of the actual value, respectively. All the recoveries obtained on the 7800 ICP-MS were within the control limits. The LLICV results confirm sub-ppb reporting limits for all trace elements in the solution analyzed, and reporting limits in the 10–50 ppb range for the mineral elements.

| Element | LLICV (ppb) | Actual concentration (ppb) | Recovery (%) | ICV (ppb) | Recovery (%) |
|---------|----------------|----------------------------------|-----------------|-----------|-----------------|
| 9 Be | 0.1 | 0.111 | 111 | 50 | 98 |
| 23 Na | 50 | 55.4 | 111 | 5,000 | 102 |
| 24 Mg | 10 | 11.1 | 111 | 5,000 | 103 |
| 27 AI | 10 | 10.7 | 107 | 5,000 | 102 |
| 39 K | 50 | 44.9 | 90 | 5,000 | 101 |
| 44 Ca | 50 | 59.9 | 120 | 5,000 | 93 |
| 51 V | 0.5 | 0.491 | 98 | 50 | 102 |
| 52 Cr | 0.5 | 0.491 | 98 | 50 | 103 |
| 55 Mn | 0.5 | 0.511 | 102 | 50 | 101 |
| 56 Fe | 10 | 10.3 | 103 | 5,000 | 103 |
| 59 Co | 0.1 | 0.110 | 110 | 50 | 105 |
| 60 Ni | 0.1 | 0.095 | 95 | 50 | 105 |
| 63 Cu | 0.1 | 0.105 | 105 | 50 | 106 |
| 66 Zn | 0.5 | 0.435 | 87 | 50 | 106 |
| 75 As | 0.1 | 0.099 | 99 | 50 | 103 |
| 78 Se | 1 | 0.955 | 96 | 50 | 103 |
| 95 Mo | 0.1 | 0.098 | 98 | 50 | 105 |
| 107 Ag | 0.1 | 0.104 | 106 | 50 | 105 |
| 111 Cd | 0.1 | 0.101 | 101 | 50 | 104 |
| 121 Sb | 0.1 | 0.095 | 95 | 50 | 102 |
| 137 Ba | 0.1 | 0.114 | 114 | 50 | 99 |
| 201 Hg | 0.1 | 0.109 | 109 | 1.1 | 107 |
| 205 TI | 0.1 | 0.109 | 109 | 50 | 103 |
| 208 Pb | 0.5 | 0.490 | 98 | 50 | 102 |
| 232 Th | 0.1 | 0.108 | 108 | 50 | 101 |
| 238 U | 0.1 | 0.105 | 105 | 50 | 102 |

| Table 4. LL | ICV and | ICV | concentrations | and | recoveries |
|-------------|---------|-----|----------------|-----|------------|
|-------------|---------|-----|----------------|-----|------------|

ISTD recovery

In total, 308 samples and 81 calibration standards (CalStd) and QC samples were analyzed over 10 hours and the ISTD recoveries are shown in Figure 4. The red dotted lines represent upper and lower control limits of $\pm 30\%$. All the

ISTD recovery plots were within the limit specified in EPA 6020A (>70%). While there is no upper limit for ISTD recovery specified in EPA 6020A, 130% is displayed as the upper control limit on the stability plot. No internal standard failures occurred throughout the run. Because of the high matrix tolerance of the 7800 ICP-MS, the ISTD signals remained consistent throughout the run, with little variation between the different sample matrices. Also, there was no signal drift throughout the course of the sequence and no divergence in the signals for low- and high-mass ISTD elements. These results indicate no matrix accumulation on the interface or lenses during the entire sequence.



Figure 4. ISTD stability for 389 samples measured during the 10-hour run. The ISTD recoveries are displayed relative to the calibration blank. Due to limited space, not all sample names are shown in the X-axis labels.

CCV recoveries

The continuing calibration verification (CCV) sample was prepared at a concentration near the midpoint of the calibration curve (trace elements: 50 ppb, mineral elements: 5000 ppb, and Hg: 1 ppb, which is the same as the ICV). A Periodic QC block containing CCB, LLCCV, and CCV samples was analyzed automatically after every 10 normal samples, giving a total of 29 repeats of the Periodic Block. Method 6020A stipulates that CCV recoveries must be within $\pm 10\%$. If the recovery is outside the limit, the instrument must be recalibrated and the samples since the last successful CCV must be reanalyzed. All elements met the QC recovery criteria, as illustrated in Figure 5.



Figure 5. CCV recoveries over the course of the sequence.

CRM recoveries

The six certified reference samples were analyzed repeatedly in the "Samples" block (see Figure 1). NIST 1640a was analyzed undiluted and 10x diluted, while the other reference materials were analyzed after both 10x and 50x dilutions. The data shown in Table 5 was taken from the undiluted NIST 1640a and the 10x dilutions of the other CRMs. Each sample was measured multiple times over the sequence. The mean concentration, percent relative standard deviation (% RSD), and mean recovery were calculated for each analyte (Table 5). All the recoveries were within $\pm 10\%$. Not all reference materials are certified for all analytes – NA indicates the absence of a certified value.

Table 5. Mean measured values, %RSDs, and mean recoveries for all certified elements in six CRMs.

| | NIST 1640a (n=10) | | | River Se | ediment A (1 | /10, n=10) | River Sediment B (1/10, n=10) | | |
|---------|-------------------|------|---------------------|-------------------|--------------|---------------------|-------------------------------|------|---------------------|
| Element | Mean conc, ppb | %RSD | Mean recovery, % | Mean conc, ppb | %RSD | Mean recovery, % | Mean conc. (ppb) | %RSD | Mean recovery, % |
| 9 Be | 2.78 | 5.2 | 93 | 0.012 | 34.4 | NA | 0.013 | 21.9 | NA |
| 23 Na | 3,230 | 2.6 | 103 | 5,030 | 1.0 | 96 | 5,240 | 1.3 | NA |
| 24 Mg | 1,090 | 2.8 | 103 | 7,130 | 1.3 | 98 | 12,500 | 2.0 | 102 |
| 27 AI | 58.0 | 4.4 | 110 | 25,800 | 2.0 | 104 | 62,400 | 2.3 | 102 |
| 39 K | 541 | 3.2 | 93 | 14,600 | 0.8 | 101 | 19,800 | 0.5 | 106 |
| 44 Ca | 5,440 | 2.4 | 97 | 29,700 | 0.8 | 104 | 30,400 | 0.7 | 103 |
| 51 V | 15.3 | 2.3 | 102 | 25.6 | 0.7 | 101 | 100 | 0.6 | 105 |
| 52 Cr | 41.3 | 2.4 | 103 | 31,400 | 1.0 | 101 | 1,550 | 0.6 | 101 |
| 55 Mn | 41.1 | 2.6 | 103 | 801 | 1.0 | 100 | 603 | 0.8 | 106 |
| 56 Fe | 40.3 | 3.0 | 110 | 124,000 | 1.2 | 101 | 41,700 | 1.0 | 102 |
| 59 Co | 21.4 | 2.4 | 106 | 10.9 | 1.0 | 101 | 16.5 | 0.8 | 104 |
| 60 Ni | 26.6 | 2.1 | 106 | 52.8 | 1.0 | 101 | 52.2 | 0.9 | 110 |
| 63 Cu | 87.3 | 2.4 | 103 | 100 | 1.4 | 98 | 98.6 | 1.0 | 106 |
| 66 Zn | 55.8 | 2.1 | 101 | 1,470 | 0.9 | 100 | 484 | 0.7 | 102 |
| 75 As | 7.94 | 2.9 | 99 | 59.5 | 0.7 | 102 | 19.9 | 0.8 | 103 |
| 78 Se | 19.3 | 2.4 | 97 | 1.88 | 7.7 | 94 | 0.927 | 16.1 | 104 |
| 95 Mo | 46.4 | 2.3 | 102 | 0.077 | 9.8 | 94 | 0.072 | 11.1 | 90 |
| 107 Ag | 7.95 | 1.9 | 99 | 0.168 | 3.7 | 98 | 0.069 | 6.0 | NA |
| 111 Cd | 3.93 | 1.9 | 99 | 10.2 | 0.9 | 99 | 3.14 | 1.7 | NA |
| 121 Sb | 4.96 | 3.1 | 98 | 51.0 | 1.1 | 100 | 4.17 | 1.6 | 96 |
| 137 Ba | 144 | 1.8 | 96 | 49.1 | 1.4 | 100 | 401 | 1.2 | 99 |
| 201 Hg | 0.017 | 53.7 | NA | 0.006 | 63.0 | NA | 0.006 | 61.6 | 102 |
| 205 TI | 1.55 | 2.3 | 96 | 0.980 | 1.2 | 101 | 1.01 | 1.3 | NA |
| 208 Pb | 12.1 | 2.5 | 100 | 693 | 0.5 | 99 | 205 | 0.5 | 105 |
| 232 Th | 0.002 | 66.9 | NA | 2.07 | 0.8 | 102 | 10.5 | 0.9 | 102 |
| 238 U | 25.2 | 2.6 | 100 | 1.04 | 1.8 | 102 | 3.19 | 0.9 | 105 |

NA: not applicable since no reference value

Table continues...

| | Estuarian Sediment (1/10, n=10) | | | S | oil A (1/10, n | i=10) | Soil B (1/10, n=10) | | |
|---------|---------------------------------|------|---------------------|-------------------|----------------|---------------------|---------------------|------|---------------------|
| Element | Mean conc, ppb | %RSD | Mean recovery, % | Mean conc, ppb | %RSD | Mean recovery, % | Mean conc. (ppb) | %RSD | Mean recovery, % |
| 9 Be | 1.79 | 4.9 | 105 | 0.019 | 17.9 | NA | 0.015 | 43.5 | NA |
| 23 Na | 20,500 | 1.5 | 100 | 7,100 | 1.8 | 96 | 10,000 | 1.8 | 93 |
| 24 Mg | 10,300 | 1.9 | 100 | 7,180 | 2.0 | 98 | 8,130 | 2.0 | 94 |
| 27 AI | 70,500 | 2.4 | 104 | 50,600 | 2.2 | 104 | 70,000 | 2.0 | 101 |
| 39 K | 14,400 | 1.1 | 102 | 19,300 | 1.1 | 101 | 20,000 | 0.9 | 98 |
| 44 Ca | 7,900 | 1.1 | 105 | 34,300 | 1.0 | 103 | 12,200 | 0.8 | 101 |
| 51 V | 100 | 0.9 | 103 | 10.0 | 1.7 | 101 | 78.4 | 1.2 | 98 |
| 52 Cr | 81.6 | 1.2 | 103 | 0.719 | 26.6 | NA | 39.6 | 1.6 | 97 |
| 55 Mn | 397 | 1.1 | 102 | 10.6 | 1.4 | 101 | 9,960 | 1.4 | 99 |
| 56 Fe | 36,300 | 1.1 | 104 | 20,200 | 1.4 | 101 | 35,800 | 1.1 | 98 |
| 59 Co | 10.4 | 1.4 | 104 | 0.093 | 6.9 | NA | 10.2 | 1.3 | 98 |
| 60 Ni | 30.9 | 1.5 | 106 | 30.4 | 0.9 | 101 | 20.6 | 1.5 | 99 |
| 63 Cu | 19.5 | 1.4 | 100 | 28.8 | 1.3 | 97 | 292 | 1.4 | 97 |
| 66 Zn | 144 | 0.9 | 100 | 96.1 | 1.1 | 99 | 6,680 | 0.8 | 96 |
| 75 As | 9.80 | 1.1 | 100 | 19.5 | 1.6 | 101 | 583 | 1.0 | 97 |
| 78 Se | 4.62 | 5.1 | 102 | 0.966 | 13.3 | 93 | 0.058 | 68.3 | NA |
| 95 Mo | 0.054 | 6.7 | NA | 0.058 | 10.9 | NA | 0.078 | 9.7 | NA |
| 107 Ag | 0.030 | 10.6 | NA | 0.030 | 8.3 | NA | 0.033 | 7.0 | NA |
| 111 Cd | 0.308 | 3.0 | NA | 0.566 | 2.7 | NA | 20.3 | 1.2 | 94 |
| 121 Sb | 0.543 | 7.0 | NA | 3.10 | 2.0 | 100 | 40.1 | 1.3 | 95 |
| 137 Ba | 0.108 | 16.6 | NA | 488 | 0.9 | 98 | 681 | 0.7 | 95 |
| 201 Hg | 0.006 | 53.9 | NA | 0.005 | 70.3 | NA | 0.007 | 51.5 | NA |
| 205 TI | 0.006 | 26.8 | NA | 0.005 | 32.0 | NA | 0.026 | 5.9 | NA |
| 208 Pb | 30.3 | 1.0 | 100 | 40.2 | 0.5 | 99 | 5,870 | 0.7 | 96 |
| 232 Th | 10.3 | 1.0 | 100 | 10.2 | 1.1 | 100 | 10.3 | 0.9 | 100 |
| 238 U | 0.006 | 17.3 | NA | 1.03 | 2.0 | 100 | 26.0 | 1.0 | 101 |

Table 5 continued.

NA: not applicable since no reference value

Matrix spike recoveries

Representative Matrix Spike (MS) and Matrix Spike Duplicate (MSD) sample results for Soil A are given in Table 6. As specified in EPA 6020A, the spike recovery limits were set to $\pm 25\%$. If the measured spike concentration is outside the limit, the sample must be diluted and analyzed again. Soil A contains Al, K, Ca, and Fe at a higher concentration than the spike amount, so no spike recoveries are given for these elements. However, the CRM recovery results (Table 5) show that these elements can be analyzed at high concentrations with good accuracy.

Recoveries for all other elements were within $\pm 10\%$ of the true spike level, demonstrating that the accuracy of the method easily meets the EPA method requirements. The relative percent difference (RPD) was calculated between the MS and MSD recoveries. All elements met the required RPD limit of 20% defined in EPA 6020A.

| Element | Soil A conc (ppb) | Soil A MS conc (ppb) | Soil A MSD conc (ppb) | Spike (ppb) | Soil A MS recovery (%) | Soil A MSD recovery (%) | RPD MS/MSD (%) |
|---------|----------------------|-------------------------|-----------------------------|----------------|------------------------------|-------------------------------|-------------------|
| 9 Be | 0.019 | 9.24 | 9.46 | 10 | 92 | 94 | 2.3 |
| 23 Na | 6,950 | 7,930 | 7,850 | 1,000 | 98 | 90 | 8.3 |
| 24 Mg | 6,970 | 7,940 | 7,870 | 1,000 | 97 | 90 | 7.1 |
| 27 AI | 48,600 | 48,900 | 48,200 | - | NA | NA | NA |
| 39 K | 19,200 | 20,200 | 19,900 | - | NA | NA | NA |
| 44 Ca | 33,800 | 35,000 | 34,900 | - | NA | NA | NA |
| 51 V | 9.85 | 19.8 | 20.1 | 10 | 99 | 103 | 3.4 |
| 52 Cr | 1.09 | 10.9 | 10.6 | 10 | 98 | 95 | 2.5 |
| 55 Mn | 10.4 | 20.3 | 20.3 | 10 | 99 | 99 | 0.3 |
| 56 Fe | 19,800 | 21,000 | 21,000 | - | NA | NA | NA |
| 59 Co | 0.095 | 10.3 | 10.1 | 10 | 102 | 100 | 1.3 |
| 60 Ni | 30.5 | 40.2 | 40.5 | 10 | 97 | 100 | 2.9 |
| 63 Cu | 29.6 | 39.1 | 39.7 | 10 | 95 | 101 | 5.7 |
| 66 Zn | 97.6 | 203 | 208 | 10 | 105 | 110 | 4.5 |
| 75 As | 20.0 | 29.4 | 29.9 | 10 | 94 | 99 | 5.3 |
| 78 Se | 1.01 | 10.2 | 9.85 | 10 | 92 | 88 | 3.8 |
| 95 Mo | 0.072 | 10.2 | 10.4 | 10 | 101 | 103 | 1.6 |
| 107 Ag | 0.034 | 10.1 | 10.3 | 10 | 100 | 103 | 2.4 |
| 111 Cd | 0.533 | 10.5 | 10.7 | 10 | 99 | 102 | 2.6 |
| 121 Sb | 3.00 | 12.7 | 13.2 | 10 | 97 | 102 | 5.2 |
| 137 Ba | 482 | 969 | 984 | 500 | 97 | 100 | 3.0 |
| 201 Hg | 0.006 | 0.205 | 0.221 | 0.2 | 100 | 108 | 7.8 |
| 205 TI | 0.004 | 10.2 | 10.3 | 10 | 102 | 103 | 1.1 |
| 208 Pb | 40.1 | 50.6 | 50.3 | 10 | 106 | 102 | 3.3 |
| 232 Th | 10.0 | 20.5 | 20.6 | 10 | 105 | 106 | 1.5 |
| 238 U | 1.01 | 11.3 | 11.4 | 10 | 103 | 103 | 0.9 |

Table 6. Matrix Spike (MS)/Matrix Spike Duplicate (MSD) spike concentrations, recoveries, and relative percent differences (RPD) for 1/10 Soil A.

Conclusions

This study shows that long-term sequences of typical, varied environmental sample digests can be analyzed with good accuracy, precision, and excellent long-term stability using the Agilent 7800 ICP-MS. This performance was achieved using He mode for the removal of polyatomic interferences, combined with HMI for exceptional plasma robustness and matrix tolerance.

ICP-MS MassHunter software uses powerful and intuitive method setup and data analysis/reporting tools to help the operator to generate new batch methods and quickly process results. This simplifies the task of method development, routine operation, and data interpretation, while ensuring consistent operation in busy laboratories. Agilent's ISIS 3 is ideally suited to high throughput applications. The ISIS pump loads samples/rinse solutions quickly, and discrete sampling reduces the analytical cycle time by overlapping the acquisition and rinse time. It also reduces the amount of time that sample matrix is being introduced into the instrument, providing superior stability, minimizing QC errors, and reducing system maintenance.

Using the configuration described, the sample analysis time per sample can be reduced by 50% compared to conventional ICP-MS systems.

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More Information

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